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TRANSACTIONS

OF THE

AMERICAN INSTITUTE OF MINING

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(INCORPORATED)

IRON AND STEEL DIVISION

1930

PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT
MEETINGS HELD AT NEW YORK, FEBRUARY, 1930, AND AT
CHICAGO, SEPTEMBER, 1930

Notice

This volume is the third of a series constituting the official proceedings of the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers. It contains papers and discussions presented at the New York Meeting, Feb. 17–20, 1930, and the Chicago Meeting, Sept. 22–26, 1930.

Papers on iron and steel subjects are to be found in many volumes of the TRANSACTIONS of the Institute; during the past 25 years in Vols. 37 to 45, inclusive, 47, 50 and 51, 53, 56, 58, 62, 67 to 71, inclusive, 73 and 75 Vol. 67 was devoted exclusively to iron and steel.

Iron and steel papers published in the TRANSACTIONS may be found by consulting the general indexes to Vols. 1 to 35 (1871–1904), Vols. 36 to 55 (1905–1916), and Vols. 56 to 72 (1917–1925), and the indexes in succeeding volumes.

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The Howe Memorial Lecture

By the death of Henry Marion Howe on May 14, 1922, the Institute lost one of its most distinguished members and past-presidents. Howe was a commanding figure in the field of metallurgy and his great achievements brought him recognition from many scientific and technical societies as well as from several governments. These included the Bessemer, John Fritz and Elliott Cresson medals, the cross of Chevalier of the Legion of Honor of France and of the Order of St. Stanislas (Russia). He received honorary degrees from Harvard, Lafayette, and the University of Pittsburgh. He was the first metallurgist to be elected member of the National Academy of Sciences.

Howe joined the American Institute of Mining Engineers in 1871, the first year of its existence, and for a period of nearly fifty years he contributed to its growth and to its fame as no other member has done.

It was most fitting that steps should have been taken to keep his memory alive as an inspiration to future generations of workers and students in the field of his extraordinary activity and productiveness. The Howe Memorial Lecture was consequently authorized in April, 1923, as an annual address to be delivered by invitation under the auspices of the Institute by an individual of recognized and outstanding attainment in the science and practice of iron and steel metallurgy or metallography, chosen by the Board of Directors upon recommendation of the Iron and Steel Division. In conformity with a decision of the Iron and Steel Division, the past lecturers have so far constituted the Nominating Committee. In the selection of the lecturers, the members of the Nominating Committee have been guided to a certain extent by their personal associations with Professor Howe during his lifetime.

So far, only American metallurgists have been invited to deliver the Howe lecture. It is believed that this lecture would gain in importance and significance were it possible to include metallurgists from other countries, but the Institute has not yet been able to do this on account of lack of special funds to support this lectureship.

The titles of the lectures and the lecturers are as follows:

1924 What is Steel? By Albert Sauveur.
1925 Austenite and Austenitic Steels. By John A. Mathews.
1926 Twenty-five Years of Metallography. By William Campbell.
1927 Alloy Steels. By Bradley Stoughton.
1928 Significance of the Simple Steel Analysis. By Henry D. Hibbard.
1929 Studies of Hadfield's Manganese Steel with the High-power Microscope. By John Howe Hall.
1930 The Future of the American Iron and Steel Industry. By Zay Jeffries.
1931 The lecturer will be Francis F. Lucas.

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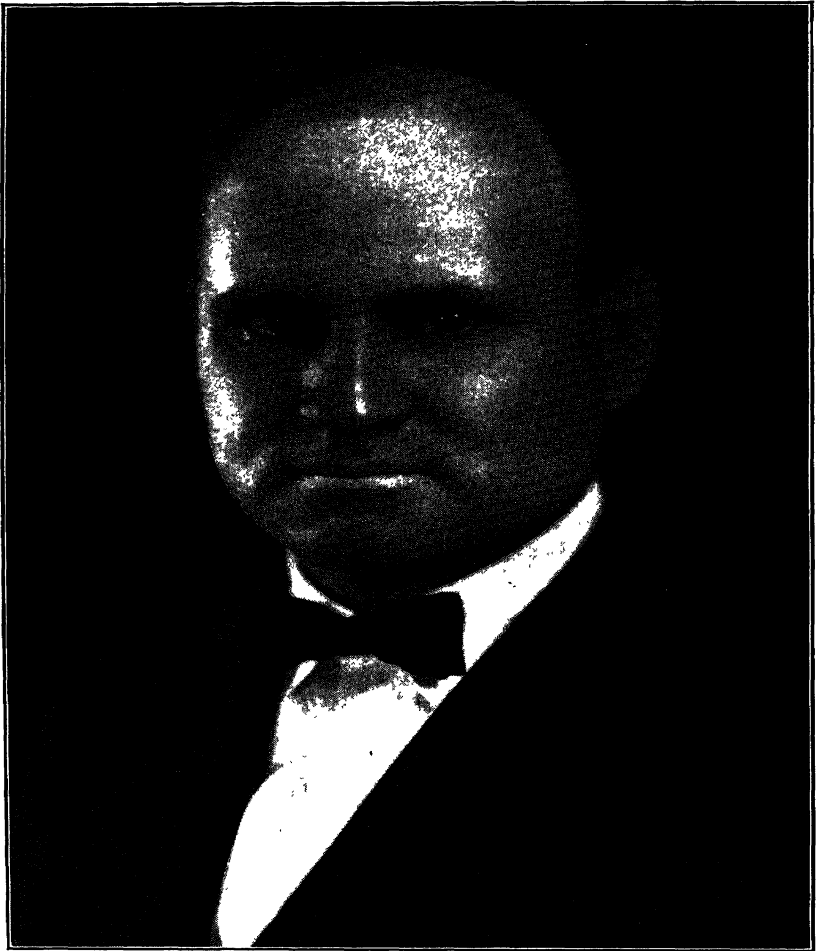
ZAY JEFFRIES

Henry Marion Howe Memorial Lecturer, 1930

The Future of the American Iron and Steel Industry

By Zay Jeffries,* Cleveland, Ohio

THE history of the development of our great iron and steel industry has been recorded in many publications, not the least important of which are the TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers. During the life of the Institute, of less than 60 years, the annual production of pig iron in the United States has increased more than 23 times. Such a rate of growth may seem small when compared with that of the automotive industry, which has increased 100 times in the last 20 years, or when compared with the growth of other industries of recent birth. The comparison appears less unfavorable, however, when the fact is taken into consideration that the iron and steel industry has existed on the earth in some form for thousands of years.

The trade journals, the Department of Commerce and technical societies keep us currently informed concerning technical and corporate developments and the statistics of the American iron and steel industry. Merely to describe the high spots of the industry as it exists today would require a book of no small size. It involves the utilization of about 900,-000 people, the payment of $1,400,000,000 in annual wages and salaries, the investment of $14,000,000,000, the mining annually of 70,000,000 tons of iron ore, 15,000,000 tons of limestone, and 120,000,000 tons of coal. It results in the production of 40,000,000 long tons of pig iron and 50,000,-000 long tons of steel ingot. In addition, the industry includes ownership and operation of railroads and steamship lines, the production of cement, timber, coke, gas, by-products, and many other activities.

The leading part played by the iron and steel industry in promoting the confidence of the public in corporations and corporate management is well known. The industry has also provided worthy examples of vertical integration and mass production. The social activities within the industry have been no small factor in promoting the fuller development and greater happiness of the American working man and his family. In this connection I advise reading a paper by Theodore W. Robinson,[1] which

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* Consultant, Aluminum Company of America; Incandescent Lamp Department of General Electric Co. and National Tube Co.

[1] T. W. Robinson: The Economic and Social Development of the American Iron and Steel Industry. *Jnl.* Iron and Steel Inst. (1927) **116**, 13.

was published in the Journal of the Iron and Steel Institute of Great Britain.

SCIENCE OF PREDICTION

The past has been necessary, interesting and romantic and the successes and failures provide a solid foundation for continued building. No matter with what satisfaction the past can be viewed, however, it is the potentiality or future which gives us most concern. The great scientist, teacher, writer and philosopher, Henry Marion Howe, in memory of whom this lecture is given, delighted to speculate about the future. In his monumental book, "The Metallography of Steel and Cast Iron," he philosophized concerning a hypothetical "ether mill" which the inhabitants of the earth might be able some day to use. The idea was that man might be able to tap the energy of motion of the earth in its orbit around the sun and as a consequence the earth would move nearer to the sun. Many of his speculations were of such practical nature as to provide effective stimulation of thought among a large number of people with inevitable beneficial results. The previous Howe lecturers have discussed several phases of metallurgy and metallography in which Professor Howe was himself actively interested. By devoting this hour to a discussion of some phases of the future of the American iron and steel industry, we will be emphasizing another of Professor Howe's interests and especially one for which he gave much of his valuable energy during his last days.

Opinions regarding the near future are given periodically by Messrs. Schwab, Farrell, Campbell and others. Statements made by these officials of large industrial corporations are based on a number of things, including the general business conditions, forward orders and customers' stocks. In addition, the trade journals and statistical organizations, by analysis from many facts, provide us with predictions for the near future with sufficient accuracy to justify the contention that there is developing a science of prediction. Important and valuable as is this service, I mention it only in passing to conserve time for the consideration of the outlook for the more distant future.

SUPPLY OF RAW MATERIALS

At the outset it can be stated with certainty that there is ample iron in the earth's crust for all possible future needs. The earth's crust contains about 5 per cent. iron. It is only natural that ores geographically accessible, rich in iron, relatively free from objectionable impurities and which can be mined cheaply will be used as long as they last. There are in North America sufficient reserves meeting these requirements to last another generation and when these more desirable ores are depleted there are available unlimited quantities of more inaccessible and lower

grade deposits.   There is no danger of exhausting the limestone supply, and coal reserves are sufficient to last many generations.   The richer and more extensive deposits of manganese ores are not in the United States or Canada but there is little danger of a world shortage of this element. It can therefore be definitely concluded that the supply of raw materials will not limit the growth of the American iron and steel industry.
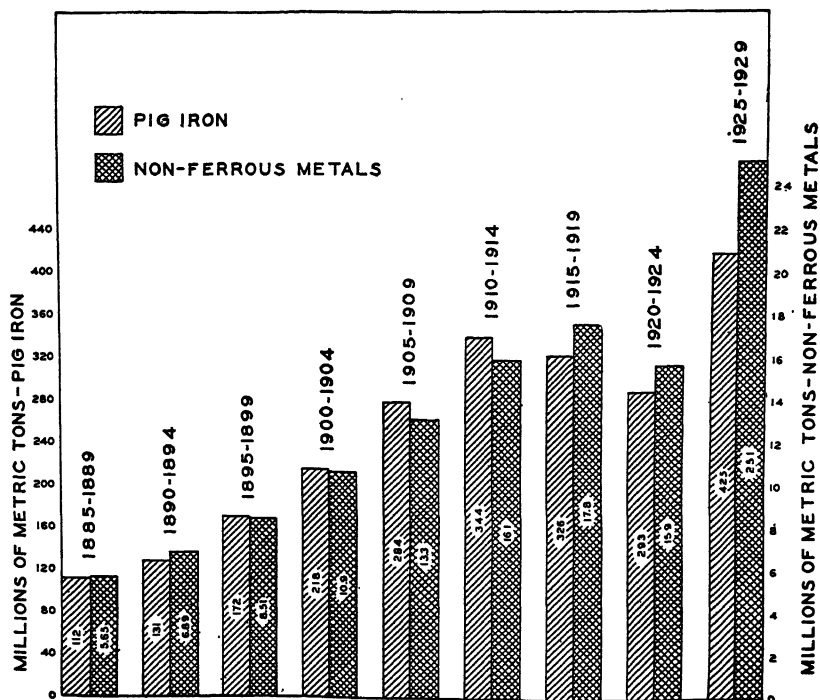
FIG. 1.—WORLD PRODUCTION OF PIG IRON AND NON-FERROUS METALS SINCE 1885.

PREDOMINANCE OF IRON

The predominating position of iron in the metal industry is shown in Fig. 1.   Of the new metal produced in the world, pig iron represents about 94 per cent.   The non-ferrous metal production is represented on a scale 20 times that of pig iron for the purpose of comparison.   Manganese and chromium are not included in the non-ferrous metals production, but nickel is.   The total of non-ferrous metals has increased relative to pig iron during the last 10 years and change in this direction may be more.   A compensating factor, however, is the replacement of non-ferrous metals for some uses with the newer stainless irons and steels.

The three principal non-ferrous metals are copper, zinc, and lead. The earth's crust, according to F. W. Clarke,[2] contains only 0.01 per

2 F. W. Clarke: The Data of Geochemistry.   U. S. Geol. Survey, *Bull.* 770 (1924).

cent. copper, 0.004 per cent. zinc and 0.002 per cent. lead.   The produc-
tion of these metals, even if they had the desirable characteristics of iron
and iron alloys, which in many respects they have not, on a scale neces-
sary to replace any considerable quantity of iron would seem to be improb-
able for even a short duration and practically impossible for any extended
period.   Aluminum and magnesium are not so limited in supply of raw
materials and consequently in the distant future we may look for iron
and one or both of these light metals to provide the major metal require-
ments for mankind.   There is ample supply of ores of the other metals,
however, to last under present rates of expansion for several decades and
it seems unlikely that any of the metals will ever be exhausted.   Because
of the inexhaustibility of iron in the earth's crust, the great fitness of iron
and its alloys for man's needs, the higher cost and limited quantities of
the chief non-ferrous metals, the high cost and for many purposes, lack
of fitness of aluminum and magnesium, it would seem to be a safe con-
clusion that in 20 years the iron production of the world will be at least
10 times that of all non-ferrous metals combined.

There is a point in this connection, however, which may be stressed.
Although the various metals are competing with one another for certain·
applications, one metal may be clearly superior for other uses.   For
example, aluminum competes with cast iron for internal-combustion
motor pistons but steel has no competition for rails.   Each metal has
gained its present position against severe competition.   Each has such
a variety of uses that a condition of substantial temporary stability,
obtains.   Each metal supplies certain needs more economically than
any other and by so doing helps to perfect our industrial machinery and
to promote continued expansion in many directions.   Copper has been
indispensable to the electrical industry, yet the gain in iron production
as the direct result of the judicious use of copper has been even greater
in tons than the whole of the copper production.   In a similar manner
we should regard all of the materials, whether metallic or non-metallic,
organic or inorganic, as cooperating toward a sounder economic structure.

One of the non-metallic competitors of iron and steel is concrete,
which has in recent years substituted for steel in many places.   The
relative rates of growth of the iron and portland cement industries in the
United States are given in Fig. 2.   For comparison, the rate of increase
of population is also charted.   Since 1885 the population has increased
about 2.1 times.   The pig-iron production has increased from about
4,000,000 to about 40,000,000 gross tons annually from 1885 to 1929 and
the output of portland cement in the same period has increased from
about 30,000 to 30,000,000 gross tons annually.   Thus the iron produc-
tion has increased about 5 times as fast as the population and the portland
cement production about 100 times as fast as iron.   In fact, there are
more cubic feet of cement produced in the United States now than of

|iron and a greater tonnage of concrete is poured annually than of pig
iron.   Yet I am inclined to believe that there are more tons of pig iron
produced currently than there would be if we had no cement or concrete.
The steel which concrete has replaced in certain types of construction is
probably made up by added consumption in the automotive industry
alone, as a result of the superior fitness of concrete in road construction.
Furthermore, each of us is able to have more because of the cement indus-
try and this makes us better customers, directly and indirectly, for iron
products.   Concrete and other non-metallic materials like lumber and
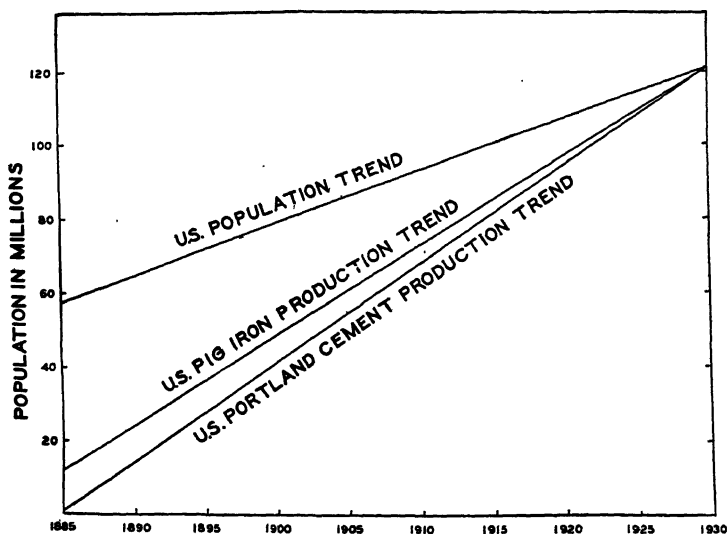
FIG. 2.—AVERAGE PRODUCTION TRENDS OF PIG IRON AND PORTLAND CEMENT FOR
UNITED STATES.
Pig iron increased from about 4,000,000 tons in 1885 to 40,000,000 tons in 1929, and
portland cement from about 30,000 tons in 1885 to 30,000,000 tons in 1929.

clay products have been competing with iron for many years and there
seems no possibility of substitution for many important applications.
But if one important material, in part competitive, like cement, can grow
100 times faster than the iron industry and the latter still show healthy
and relatively rapid growth, it seems unlikely that the continued growth
will be prevented by anything which may happen in the non-metallic
materials industry.

ECONOMICAL APPLICATIONS OF IRON AND STEEL

While it would thus appear that the iron and steel industry is basically
well fortified against competition from either metallic or non-metallic
materials, there are some factors that need careful consideration.   In the
first place, research and development in the iron and steel industry should
keep pace with similar activities in other industries.   It is perhaps not

wise to put too much effort in attempting to apply iron and steel in places where other materials seem clearly better suited. On the other hand, it is the problem of the iron and steel industry to ascertain the applications where iron or iron alloys can serve most economically. There is no way to accomplish this save by aggressive research and development. Americans can be proud of their past achievements in the direction of labor-saving devices and in general of the mechanical engineering of the industry from ore to finished product. Recent developments like the blast furnace of large capacity, the welding of tubular products, continuous sheet rolling, stretch rolling, and the manufacture of coiled strip tin plate, bear evidence that this work is not now being neglected. There is, however, much to be done in the future along these lines and continued activity in this field is necessary in order to keep the iron and steel industry in a healthy condition.

Many of the new metallurgical developments are coming to us from abroad. In recent years the stainless steels, the nitriding process and nitriding steels, and Izett steel have had their major developments from the research angle, in Europe. I suspect this is in part the result of the cumulative effect of research carried out over a long period of time. Reassuring for the future of metallurgical improvements in America are the joint research now in progress under the direction of Dr. Herty and sponsored by the U. S. Bureau of Mines, the Carnegie Institute of Technology and several industrial corporations; the expansion of research in the U. S. Steel Corporation as well as in most of the other large units; the formation of the Alloys of Iron Research under the direction of Dr. Waterhouse; the initiation of work at the Battelle Memorial Institute under Dr. Gillett; the continued activity of various government departments and universities; the activities of technical societies and trade journals; and last but not least a solid foundation of science on which to build. I think we may conclude that in the field of metallurgical research, the American iron and steel industry, even though it may not have been as active as might have been desired in the past, faces the future with bright prospects.

POTENTIAL CHANGES

But in spite of anything research, management or salesmanship can accomplish, we may expect changes which will affect the iron and steel industry for better or for worse. The industry should try, in so far as is possible, to anticipate the effect of potential changes and to accommodate itself to them. Let us consider a few possibilities and in doing so give poetic license to our imaginations.

1. *The Iron Age* (Jan. 2, 1930) estimates that 35 per cent. of the steel consumed in the United States in 1929 was used by the automotive and railroad industries. Of course, much of this can not be replaced by any

other metal, but a considerable tonnage must be moved about and energy is consumed in so doing. It is not unreasonable to suppose that as the cost of power increases, relatively, there will be a greater incentive to reduce weights of automotive vehicles and rail cars. This condition, at present, points to the use of more tubular structures and in many cases to light alloys. Perhaps the next 5 or 10 years may not witness much change, but is not such a direction of change eventually inevitable?

2. It now seems probable that the healthful ultra-violet rays of the wave lengths obtained in sunlight can be readily provided in the future artificially. Such radiation would be produced in intensities sufficiently strong to benefit health and not too strong to cause harm. May not such a development throw the balance, already nearly ready to change, toward a new type of construction for some of our buildings? The ordinary or even extraordinary window has many deficiencies. It is not always effective in letting in light; the room is usually either too dark or too light. It is a source of drafts and usually makes for uneven temperature. It lets in the rain, snow, dust and insects. It is easily broken and often hard to open and close. It increases fuel bills and often foils privacy and in some cases it provides a too ready means of exit in case of a stock market crash. It also provides a popular burglar entrance. These objections would be largely eliminated by eliminating windows. Artificial light, artificial sunlight, and artificial ventilation would permit the use of cheaper construction, completely enclosed rooms free from drafts, uneven temperature, city noises and other disturbances. Such rooms would be cool in summer and warm in winter. Buildings could be built of any desired size and especially of large size. How would such a change affect the iron and steel industry? There would be less steel used for a given volume of building space and the amount of heat used would be enough less to reduce the amount of coal, which would in turn reduce the iron and steel requirements in the coal-mining and railroad industries. Although there would be some extra steel used in connection with the greater consumption of electricity, the net result would be a reduction in total iron and steel consumption for a given building space.

3. We have already witnessed the development of a huge communication industry and we can be certain that more iron and steel have been consumed than there would have been without this industry. Perhaps the next phases of the industry which may have a decided bearing on our industrial life are facsimile transmission and television. Facsimile transmission will permit the sending of information by the page as readily as is done now by the word. Photographs and diagrams can be sent with ease and with no mistakes. It transmits Chinese as easily as English. It can be transmitted either through the ether by radio or by wire. The transit speed is about 186,000 miles per second. By transmitting the master copy in this manner the same newspaper could be published in

every part of the country at about the same time. Can there be any reasonable doubt that much of the mail of the future will be sent in this manner?

One method of facsimile transmission is photographing the television image. The whole field of television opens up so many possibilities for profound change in our methods of doing things that we should try to follow it as closely as possible. By using only knowledge and apparatus now available, it would be possible for one to attend a board meeting for any hour, say between two and three o'clock in New York, another meeting from two to three in Chicago, another from two to three in Denver and another from two to three in San Francisco on the same day and all the while be comfortable in the Adirondacks, if in summer, or in the South if in winter. Although it would cost a considerable amount to do this, I am sure the inherent cost would be less than that which would be required for the trip by rail or otherwise and no form of transportation can compete with the speed. We might also visualize the future executive living in Chicago having a face-to-face talk with a person in New York one minute and in San Francisco the next. Aside from the advantage of compressing distance, the system would remove the hazard of fistic combat and make harmless the odors from foul cigars. Just as many business trips are now avoided by the telephone and telegraph, is it not probable that many more in the future will be made by sending the people, through wires or ether, in image but with synchronous voice connection?

4. As time goes on an increasing amount of iron and steel is used in machinery and devices for handling snow. The chemical companies are working on the snow-removal problem from another angle; namely, melting it with calcium chloride or other salts. Also, gas companies are melting snow and ice in critical places. It is certain that snow in our streets, highways and railroads must be more quickly and completely removed in the future than is now the practice. It is important to the iron and steel industry to know whether the mechanical or chemical method will be more economical. I would not be surprised to see the chemical method gain the upper hand. If so, it would be only one of many examples in which mechanical processes, usually utilizing much steel, have given way to the chemical, using less steel.

5. For the last example, I will quote from a paper by E. W. Rice, Jr.:[3]

The vacuum tube rectifier may prove to be of great economic advantage in connection with the transmission of power. These tubes may be used to convert the high-tension alternating current into high-tension direct current, which can be transmitted to a receiving station where an inverted vacuum rectifier, known as a 'thyratron,' will change the direct current back into alternating current. Such high voltage vacuum tubes give promise of not only being useful for transmission of large amounts of power to extremely long distances such as 500 to 1000 miles, but may have an

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[3] E. W. Rice, Jr.: Recent Economic Developments of Electric Power. *General Electric Review* (1929) **32**, 583.

important application in large cities. In many cases the vacuum tube rectifier and thyratron system may increase by two or three times the useful power capacity of existing underground cables. The investment in such cables runs now into many millions of dollars and any practical method of multiplying their output will prove of unusual economic importance.

This development may revive the old suggestion to locate electric power plants near the coal mines or oil or gas wells and transmit more power through wires and relatively less on wheels, with the use of less iron and steel per unit of power transmitted.

EFFECT OF NEW DEVELOPMENTS

Many other possible changes could be mentioned, representing potentialities of things already known, and certainly there will be a continuous flow of new ideas. New ideas can be expected in somewhat increasing numbers because of the cumulative effect of the training and experience of a constantly increasing research group. New ideas should, however, be still further stimulated because of the solid foundation of science on which to build. Of particular moment are the principle of relativity and the Bohr-Heisenberg Uncertainty Principle. The latter has been to an extent a child of the former and promises in some ways to be of great practical importance. Both Bridgman and Langmuir seem to agree that many of the moot problems of physics and chemistry can be classified, by means of the Bohr-Heisenberg uncertainty principle, into those which have meaning and those which have not. It also appears that much energy has been wasted in the past on meaningless questions. If this principle serves to guide our fundamental physical and chemical research in the right direction we can be assured of rapid and substantial change in the future. Any new developments which gain headway in competition with the existing system will of course represent either general economy or better service. The greater the developments and hence the greater the general economy or the greater the improvement in service, the better it will be for humanity, but the iron and steel industry may either suffer or benefit from any particular development. Because of the many advantages of iron and steel, I should expect this industry on the average to benefit from the developments which are to come. The growth of the industry may be faster in dollars than in tons, however, because of the ever-increasing demands for quality and for combinations of properties best provided in alloy steels. According to Cone, in 1909 in the United States only 1 ton of alloy steel was made for each 131.6 tons of total steel, whereas in 1928 there was 1 ton of alloy steel produced for each 16 tons total. We may, I think, expect the proportion of alloy steel to increase still further in the future.

The iron and steel industry has much yet to do in standardization and simplification. The accomplishments of the past 15 years in this direction have been great and the industry is healthier as a result.

One large steel company in the United States is working to 45,000 specifications. Other companies are proportionately burdened. Some of these specifications differ in such minute detail that it seems certain that the number could be greatly reduced with resulting over-all economy. Perhaps the American Standards Association can do much to help in future standardization, but to achieve the proper results the customers and manufacturers must cooperate toward this end.

EFFECT OF BUSINESS IN GENERAL

Important as are the various points discussed above, however, there is another factor which is most important of all; namely, the general level of business. It is now well known that the iron and steel business is good when, and only when, business generally is good. The first requisite for healthy future of the iron and steel industry is therefore a healthy general business. It should be the object of the iron and steel industry to try to promote general business health. This whole subject is so involved, economically, politically and psychologically that it might seem futile to discuss it at all in the brief time at our disposal, but even a brief discussion may serve to convince us that this is as much our problem as it is the problem of anyone and that each of us can lend a helping hand.

In 1920 and 1921 the public desired many things which it could not buy because of lack of money. The manufacturers stood ready to produce these things but did not do so because there was no demand. The laborer was anxious to work for a wage in the production of these things but could not find employment. This seems like a ridiculous situation when it is known that the producers had the energy, the raw materials, the equipment, the know-how, and the desire to produce and sell and the public had the desire to consume, but for some reason the money or credit was not in the hands of those who desired to consume. During this period even the usually faithful law of supply and demand proved to be a false guide. There was no real sugar shortage, for instance, except in people's minds. Many families, however, bought large amounts at several times what it was worth and stored it. When the facts became available it was found that there was no shortage, but an oversupply. Similarly, late in 1919 and early in 1920 industrial corporations, for some reason, acted on the assumption that there was an undersupply of a number of materials, including steel. When large amounts of such materials were purchased at high prices it was discovered, after it was too late, that instead of a shortage there was an oversupply. Statistical information now being compiled and circularized by the U. S. Department of Commerce should go far to avoid either psychological or real shortages, as well as overproduction, in the future. The producing and distributing organizations, however, must assume the burden of balancing

supply with demand. It should be the aim of the iron and steel industry to avoid large inventories of raw materials in its own stock and to watch customers' inventories closely.

We have watched the vicious cycle of decreased sales, unemployment, reduction of buying power, still further decreased sales, still more unemployment, and so on, proceed with the idea that such a cycle is normal. Furthermore, we have watched the conditions leading to this vicious cycle with a feeling that they were uncontrollable. Now, under the leadership of President Hoover, supported and assisted by some of our greatest industrialists and economists, it is positively asserted that business depressions need not be so deep nor so long; that the business depression is not a disease, mysteriously contracted and which must run its course; that the symptoms are evident in advance and preventatives can be used effectively. This is one of the most encouraging indications in the future outlook for all industry, including iron and steel.

We will perhaps all agree that no useful end is served by developing business just for the sake of having a bigger business. But business can be made not only the agency for producing and marketing goods and rendering service but the means for the development of fuller lives. Unlike a candle, which is consumed as it performs its function of giving light, a human being is better off working than idle. His muscles are so constituted that he must use them to develop them and there is no way to become efficient mentally except by doing mental work. By giving constructive employment, therefore, industry does provide an extraordinary means for the fuller development of the individual. Furthermore, the whole nation is buoyant when business is good and depressed when business is poor. Is not this an indication that the former condition is the one of health and the latter the one of sickness? The test for progress is whether or not people generally are experiencing greater satisfaction in living. We all know that good business conditions promote satisfaction in living.

Notwithstanding the past depression and peak business cycles, business as a whole has shown an average growth greater than that of the population. It is desirable to have this rate of growth continued or increased. Growth calls for extra construction and equipment to provide for the increased production and this permits us to add currently to our reserves of real wealth. Should the general business activity decline, the expansion activities would cease and industry would lose more than in proportion to the actual decline of goods produced for current consumption.

ESSENTIALS FOR BUSINESS HEALTH

Economists have partly analyzed conditions for business health and have enumerated a number of potential depression symptoms. We can be assured, for example, that our money and credit must be wisely

controlled and that our Federal Reserve system is the most effective financial stabilizer so far devised in the United States. We are warned, however, that money is not wealth but under a sound money system it can be exchanged for real wealth. International trade, giving rise to imports and exports, makes it necessary to determine the rates of exchange of our money for that of other nations. Our workmen must compete against workmen in all parts of the world. We have established a rather high standard of living; that is, a standard which consumes a large amount of commodities per capita. As one means of helping to maintain this high living standard, we impose a duty or tariff on certain imported goods, which in part is intended to protect our workmen from the competition of those in other countries living under lower standards. The tariff is also an aid to mass production, which in turn is conducive to the effective use of labor-saving devices and hence makes possible manufacturing costs so low that we can compete with other nations in many foreign markets. Thus the extent of our exports is one of the business health factors. We are urged, therefore, to think internationally.

The matter of surplus production is also important. In the agricultural industry production is not subject to exact control and consequently a grave problem in handling surpluses is forced upon us. It is hoped that the Federal Farm Board will so handle this situation as to minimize the evils. But the iron and steel industry can avoid any substantial surplus production and, for its own good as well as for that of business in general, should do so.

It appears that the two chief essentials for business health are (1) opportunity for individuals to function and (2) the determination of proper rewards for services.

With reference to the individual's opportunity to function, we have been told so often of the depressing effect of our machine age and mass production on the workers that it may seem strange to conclude that conditions were never better at any place or at any time for the individual's development than now in America. We are told that we are no longer developing mechanics as in the good old days. Why worry about developing mechanics when our present system turns out instruments and machines in countless numbers with greater precision in dimensional control than the old-time mechanic could even measure? Most of us can remember the old-time plant with few offices, many laborers who worked long and hard, small sales force, and often no engineering or research. Contrast that with a modern industrial institution. Sales forces have not only expanded tremendously but sales activities have risen to marked dignity. We depend on sales departments to educate the public and to make market surveys, which are used to improve products and balance production with consumption. Engineering and

research now occupy important places. The manufacturing is controlled by executives with much supervisional assistance. Good positions are available for lawyers, doctors, accountants, buyers, financiers, inventors, librarians, chefs, stenographers, truck drivers, policemen, detectives and so on, in addition to those who are actually producing the goods. Even in the manufacturing operation itself the number of hard-labor jobs is not great and there are more desirable supervisory positions than in the old days. With so many kinds of activity each individual has a better opportunity than under the old system to select work which he likes and in which he is proficient. There is sufficient competition for the better positions to provide a stimulus toward better work, which in itself develops the individual. In spite of the great desire of individuals to advance, however, there are always vacancies in the higher positions, a condition that provides a healthy incentive for continued individual development.

Of course, the fact that the United States comprises a large and rich area under a unified control has been largely responsible for the evolution of the present conditions. The development, however, would not have been possible except for the concentration of capital which has taken place as the result of private enterprise. Government provides general political supervision and may, although at an eventual cost, make economic mistakes which can only be slowly corrected. Concentrated capital provides economic supervision over specific industries or localities and economic laws must be ascertained and adhered to. It seems to be a fact that industries in which large concentrations of capital obtain have been most successful. They have provided the most complete service and have advanced industrial civilization most. The American iron and steel industry is particularly fortunate in this respect.

The determination of proper rewards is perhaps the most important and difficult problem before the economic world and our industrial health will improve as these rewards become more exact. The individual, for example, must have potentially large rewards to stimulate him to greater production. If some means could be worked out for properly evaluating each contribution and rewarding accordingly we could almost forget the other economic factors. Besides direct compensation to individuals, including labor, engineering, research, management, and others, there are capital, insurance, and government, both local and national, to be rewarded.

Proper rewards can be approached only by experience. For example, the increased pay of labor during the last 15 years seems to have provided greater buying power, and to have helped in giving profitable and healthful occupation to more people, which may be regarded as a proof that the change has been in the proper direction. The psychological aspects will be apparent if the time comes when labor's reward is clearly too

high and a readjustment becomes necessary for the good of all. Yet this situation must be squarely faced. It would seem, however, that these rewards cannot be accurately determined without sometimes becoming too small and sometimes too large. Inasmuch as the education of our young people is one of our most important jobs, it would seem advisable to offer greater rewards in the teaching profession in order to obtain better results. Also, government help, both national and local, should be paid more in order to promote better government. The iron and steel industry is in a position to assist in more equitable rewards for teachers and local government employees in many districts. By doing so, it would improve its own status.

The price received for a commodity is a reward. The producer of the commodity suffers if the price is either too high or too low. It is the popular belief that cut-throat competition leading to temporary low prices for a commodity is beneficial to the purchaser. Nothing could be farther from the truth. The more efficient producing units must make a profit in order to pay proper wages, to pay returns on capital invested, and to improve the business. Otherwise the prices will eventually increase. So the iron and steel industry can help in the maintenance of good business if it on the one hand avoids price wars and on the other aims at only a fair profit, and it may be mentioned in passing that no profit can be considered fair which does not generously provide for the future development of the industry.

If we refer to the depression conditions as the vicious cycle, we may refer to the opposite conditions as the state of health. Even the physical and mental health of the people are important factors in business health. People who are well have great energy and are heavy consumers of goods; they have great ability to produce and they do not fear the future from the standpoint of gaining a livelihood. The health education activities of the government, national and local, of life insurance companies and of others engaged scientifically, professionally or industrially in health maintenance may have no small bearing on our future business health.

CONCLUSIONS

Although we cannot foresee many of the specific changes that will come in the future it can be said that there are in sight no factors outside the iron and steel industry which seriously threaten its future growth. The industry, however, needs more research and development work, both to pay for sins of omission in the past and to provide aggressive but intelligent exploitation of iron and its various and wonderful alloys for the betterment of mankind. Assuming reasonable compliance with the various conditions discussed, it would appear that the American iron and steel industry can look forward toward not only a healthy but even a romantic future.

Rate of Carbon Elimination and Degree of Oxidation of Metal Bath in Basic Open-hearth Practice, II.

By Alexander L. Feild,* Lockport, N. Y.

In the light of the experimental data on equilibrium for the reaction C + FeO = Fe + CO in molten steel recently obtained by Kinzel and Egan,[1] it is necessary to revise current theories regarding the nature of equilibrium between carbon and FeO in the basic open-hearth furnace. According to the measurements of these investigators the equilibrium constant m for the above reaction for a pressure of dissolved CO equal to 1 atm. is equal to 0.0005 at 1550° C., when concentrations of carbon and FeO are expressed in percentages by weight. Their work also shows that, with the pressure of CO fixed at 1 atm., not only is the product of carbon and FeO constant, but carbon and FeO are each independently constant—a circumstance which might have been predicted from theoretical considerations. At 1550° C., carbon is constant at about 0.025 per cent. and FeO at about 0.020 per cent., with the pressure of dissolved CO equal to 1 atm., the product of these two constants being equal to the originally mentioned constant of 0.0005.

Available data on the dissolved FeO content of samples taken from the metal bath at practical slag-metal equilibrium prove that this FeO content is determined solely by temperature and the effective FeO content of the slag. The distribution constant r at 1550° C., as determined by Herty, Gaines, Larsen, Simkins, Geruso and Watkins[2] is equal to 0.0086. A slag would have to contain $\dfrac{0.020}{0.0086} = 2.3$ per cent. effective FeO or less in order to prevent the metal from containing more dissolved FeO than that required for equilibrium with CO at 1 atm. pressure. Such low percentages of FeO are never found in basic open-hearth slags at the completion of a heat when rate of carbon drop has become practi-

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[1] A. B. Kinzel and J. J. Egan: Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron. *Trans.* A. I. M. E., Iron and Steel Div. (1929) 300–319.

[2] C. H. Herty, Jr., J. M. Gaines, Jr., B. M. Larsen, W. A. Simkins, R. L. Geruso and S. P. Watkins: The Physical Chemistry of Steel-making: The Solubility of Iron Oxide in Iron. *Bull.* 34, Mining and Metallurgical Investigations, Carnegie Institute of Technology, U. S. Bureau of Mines and Advisory Boards (1927).

cally nil and practical slag-metal equilibrium obtains. Finishing slags with 15 to 30 per cent. FeO are the general rule. Hence, at practical slag-metal equilibrium the metal bath is highly overoxidized if normal oxidation is to be determined by the equilibrium typified by the reaction $C + FeO = Fe + CO$, with the CO pressure equal to 1 atm. The effect of this overoxidation, which arises from irreversible molecular diffusion of FeO from the slag into the metal, is to cause the partial pressure of dissolved CO_2 in the metal bath to rise above the normal value. The normal CO_2 pressure may be defined as the pressure that prevails when there is true equilibrium for the reaction $C + FeO = Fe + CO$. This normal pressure is so small that it may be neglected and, while the percentage increase as a result of overoxidation at practical slag-metal equilibrium is relatively large, its actual value remains relatively small as compared with the coexisting CO pressure, and for practical purposes is negligible.

The carbon content of the metal bath at practical equilibrium is much greater than might be predicted from the equilibrium constant of Kinzel and Egan. For example, with 20 per cent. effective FeO in the slag at 1550° C. and a distribution constant of 0.0086, dissolved FeO would be equal to $20 \times 0.0086 = 0.17$ per cent.; hence carbon at true equilibrium, in the sense of the reaction $C + FeO = Fe + CO$ (1 atm.), would be equal to 0.003 per cent. No such low carbon contents are ever obtained in ordinary practice. The higher carbon contents which characterize practical equilibrium can be ascribed to an increase in the pressure of dissolved CO. This increase in CO pressure does not affect the FeO content, which is determined entirely by the ratio of the CO_2 pressure to that of CO—a ratio which is always numerically small but varies over a wide range.

Practical equilibrium between carbon and FeO, therefore, is made up of two separate equilibria: (1) the distribution equilibrium of FeO between slag and metal and (2) the equilibrium for the reaction $C + FeO = Fe + CO$ with the percentage of FeO fixed by the first type of equilibrium and that of carbon determined by the supersaturation of the metal bath with CO, which results in relatively high but thermodynamically unstable CO pressures.

Release of this unstable CO pressure by mechanical stirring of the bath serves only to lower the carbon content. There is no effect on dissolved FeO, except a small transient decrease which would be quickly offset by diffusion of FeO from the slag.

While dissolved CO might build up to high pressures in a quiescent or "flat" bath, it is difficult to conceive of high CO pressures during an active carbon boil. It will be assumed in the present paper that CO pressure during a period of normal CO evolution may be taken for convenience at 1 atmosphere,

EQUATIONS GOVERNING PRACTICAL EQUILIBRIUM

In the previous paper of the same title[3] it was shown that the well known law of mass action leads directly to the relationship

$$-\frac{dx}{dt} = k(xy - m) \tag{1}$$

provided the pressure of CO is taken as unity. For reasons given above this provision does not apply to the condition of practical equilibrium. If the CO pressure in atmospheres is denoted by P, equation 1 becomes

$$-\frac{dx}{dt} = k(xy - mP) \tag{2}$$

At practical equilibrium, rate of carbon drop becomes negligibly small and hence $\frac{dx}{dt} = 0$. For this condition, therefore, equation 2 may be written

$$xy = mP \tag{3}$$

But y, the FeO content of the metal, is equal at slag-metal equilibrium to rw. Hence, at practical equilibrium

$$y = rw \tag{4}$$

and

$$x = \frac{mP}{rw} \tag{5}$$

The product xy is constant only to the degree that P is constant, or

$$xy = mP \tag{6}$$

EQUATIONS WHICH GOVERN DURING THE PERIOD OF A CARBON BOIL

For the period of a carbon boil the equations of the previous paper[4] would not appear to require any revision. The equations as developed referred to a CO pressure of 1 atm., and, as explained above, there seems to be no logical basis at present for assuming supersaturation during a carbon boil.

For a carbon boil at 1550° C., equation 1 reduces to

$$-\frac{dx}{dt} = k(xy - 0.0005) \tag{7}$$

since $m = 0.0005$ and $P = 1$.

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[3] A. L. Feild: Rate of Carbon Elimination and Degree of Oxidation of the Metal Bath in Basic Open-hearth Practice, I. Iron and Steel Technology in 1928, A. I. M. E. (1928) 114.

[4] A. L. Feild: *Loc. cit.*

Equation 7 may be rewritten as follows:

$$xy = -\frac{1}{k}\frac{dx}{dt} + 0.0005 \qquad [8]$$

Obviously, the product xy is constant during a carbon boil at constant temperature provided $\frac{dx}{dt}$, the slope of the carbon-time curve, is constant; i. e., provided the carbon-time curve is a straight line over the period in question.

The empirical nature of the constancy which may be exhibited by the product xy during a carbon boil is apparent.

Equation 3 of the previous paper holds without revision for the period of the carbon boil and also at quiescence, since it does not contain any term in P.

Equation 7 of the previous paper needs no revision for application to the period of a carbon boil. For practical equilibrium, equation 7 of the previous paper is to be modified by changing the term $\frac{CAm}{Mrx}$ to $\frac{CAPm}{Mrx}$ and the term $\frac{m}{x^2} \cdot \frac{dx}{dt}$ to $\frac{mP}{x^2} \cdot \frac{dx}{dt}$. This change arises from the fact that CO pressure at practical equilibrium is no longer taken as unity.

RATE OF CARBON DROP MORE PRECISELY DEFINED

In the previous paper, rate of carbon drop, $\frac{dx}{dt}$, was taken as the rate of disappearance of dissolved carbon. This is exactly true only so long as the CO pressure is constant. If the CO pressure is increasing, the actual rate of carbon drop is less than the rate of disappearance of dissolved carbon, since carbon is accumulating in the metal in the form of CO, which in the case of a "killed" test sample will appear in the analytical report as carbon.

Let $\frac{dR}{dt}$ = actual rate of carbon drop as determined by analysis of "killed" samples

and S = solubility of CO in per cent. by weight at pressure of 1 atmosphere.

Then $-\frac{dR}{dt} = -\frac{dx}{dt} - S\frac{dP}{dt}$ \qquad [9]

During a carbon boil $\frac{dP}{dt} = 0$ and $\frac{dR}{dt} = \frac{dx}{dt}$.

At the moment of cessation of the boil $\frac{dP}{dt}$ ceases to be equal to zero and P increases to its final maximum value; i. e., the value which has been hitherto assumed to correspond to the state of practical equilibrium.

EQUATIONS WHICH GOVERN FROM TIME OF CESSATION OF CARBON BOIL UNTIL PRACTICAL EQUILIBRIUM IS REACHED

Until the carbon boil ceases $\dfrac{dR}{dt} = \dfrac{dx}{dt}$, and at practical equilibrium $\dfrac{dR}{dt} = \dfrac{dx}{dt} = 0$. In the interim, however, $\dfrac{dR}{dt}$ is not equal to $\dfrac{dx}{dt}$. The relationship which then prevails is that indicated by equation 9, with $\dfrac{dR}{dt}$ put equal to zero, or $-\dfrac{dx}{dt} = S\dfrac{dP}{dt}$. [10]

It follows from equations 2 and 10 that, during this period of quiescence prior to attainment of final equilibrium,

$$xy = \frac{S}{k}\frac{dP}{dt} + mP \qquad [11]$$

and, by differentiation with respect to P,

$$\frac{d(xy)}{dP} = \frac{S}{k}\frac{d^2P}{dt^2} \times \frac{dt}{dP} + m \qquad [12]$$

Elementary considerations would indicate that $\dfrac{d^2P}{dt^2}$ is of negative sign. Since S, m and k are positive members and $\dfrac{dt}{dP}$ is also positive, the question of whether the product xy increases or decreases during this period of approach from boil to final equilibrium depends on the relative values of the two terms in the right-hand member of equation 12. For the special case where xy undergoes no change during increase in CO pressure,

$$m\frac{dP}{dt} = \frac{S}{k}\frac{d^2P}{dt^2} \qquad [13]$$

or, from equations 10 and 13,

$$-\frac{dx}{dt} = \frac{S}{mk}\frac{d^2x}{dt^2} \qquad [14]$$

CONCLUSIONS

Overoxidation of the metal bath during refining by the basic open-hearth process is an inherent feature. It may be reduced to a minimum only by obtaining a relatively slow rate of carbon drop and by the maintenance of a slag as low as practicable in effective FeO content. Sufficient data are not available to determine whether or not a heat is in better condition with respect to FeO during a very slow boil than it is after it has come to practical equilibrium under the "flat" slag which characterizes completion of the boil, carbon content, FeO content of slag and temperature being the same in both cases.

A New Method for Determining Iron Oxide in Liquid Steel*

By C. H. Herty, Jr.,[†] J. M. Gaines, Jr.,[‡] H. Freeman[§] and M. W. Lightner,[||]
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Few subjects have attracted the attention of metallurgists more than oxygen in steel. From the days of Mushet and Ledebur interest in this subject has been increasing, and as additional knowledge has become available, the problem has naturally grown more complex. Instead of using the simple term "oxygen" we now distinguish between iron oxide, silicates of various kinds, oxysulfides, oxygen as gas and oxygen in solid solution in steel.

There are five general methods for determining oxides in steel: hydrogen reduction; vacuum fusion; various wet-extraction methods, including electrolytic methods; methods depending on volatilization of the iron away from the oxides; and metallographic methods. For oxygen in solid steel each of these methods has both advantages and disadvantages. The hydrogen-reduction method is of no use on steels above about 0.20 per cent. carbon;[1] furthermore, it gives only FeO and possibly some MnO. The vacuum-fusion method[2] is expensive and gives total oxygen, with the exception of some Al_2O_3, and does not differentiate between the various oxides in which the oxygen exists. Most of the wet extraction methods[3] give only the more insoluble oxides SiO_2 and Al_2O_3, though the iodine method gives MnO to an uncertain degree (information that may be more misleading than no information

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1 J. R. Cain and E. Pettijohn: A Critical Study of the Ledebur Method for Determining Oxygen in Iron and Steel. U. S. Bur. Stds. *Tech. Paper* 118 (1919).

2 L. Jordan and J. R. Eckman: Gases in Metals.—II. The Determination of Oxygen and Hydrogen in Metals by Fusion in Vacuum. U. S. Bur. Stds. *Sci. Paper* 514 (1925).

3 C. H. Herty, Jr., G. R. Fitterer and J. F. Eckel: The Physical Chemistry of Steel-making: A Study of the Dickenson Method for the Determination of Non-Metallic Inclusions in Steel. *Bull.* 37, U. S. Bur. Mines, Carnegie Inst. of Tech. and Mining and Metallurgical Advisory Boards (1928).

at all). The electrolytic methods are open to the same criticism as the iodine method, but appear to be of more promise after sufficient research has been carried out on them. Volatilization methods have been worked out in Germany, but not completely enough to judge their values for all grades of steel. Metallographic methods obviously give the oxides that are insoluble but not those that are soluble in steel.

The object of the present investigation is to obtain a true value of the oxygen content of liquid steel. If the steel has not been deoxidized, the greater percentage of the oxygen is present as iron oxide in solution. Feild[4] has referred several times to the differentiation of FeO and iron silicates in liquid steel, but before the addition of deoxidizers the amount of ferrous silicates is probably very small compared to the amount of FeO present.

When undeoxidized, or partly deoxidized, steel solidifies, considerable quantities of gas are given off, of which CO is the major constituent. There has been considerable discussion as to whether this gas is derived from CO dissolved in the steel or from reaction between carbon and iron oxide at the time of solidification. This question was discussed during the presentation of a paper by Kinzel and Egan;[5] the discussion combined with the data given in that paper showed that the gas was probably derived from the reaction $C + FeO \rightleftarrows CO + Fe$, which takes place at the time of solidification. Obviously, a loss of CO on solidification would give a test piece lower in oxygen than the liquid steel from which the test was poured. With this in mind, one of the present writers suggested the precipitation of the dissolved oxygen as Al_2O_3 by deoxidation of the liquid steel with aluminum. The analogy between this method and the ordinary sulfur determination is readily seen.

DESCRIPTION OF THE METHOD

Aluminum reacts with iron oxide in steel as follows:

$$2Al + 3FeO \rightarrow Al_2O_3 + 3Fe$$
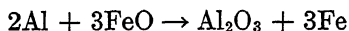
This reaction is very rapid, and results in the formation of refractory Al_2O_3 which is easily determinable by simple chemical analysis. The extent of deoxidation by aluminum has been investigated by Herty and Fitterer[6] who found the relationship (per cent. free Al)^2 (per cent. free

[4] A. L. Feild: The Physical Chemistry of Steel Making. *Metals and Alloys* (1929) 1, 279.

[5] A. B. Kinzel and J. J. Egan: Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron. *Trans.* A. I. M. E., Iron and Steel Div. (1929) 304.

[6] C. H. Herty, Jr., G. R. Fitterer and J. M. Byrns: The Physical Chemistry of Steel-making: Deoxidation of Steel with Aluminum. *Bull.* 46, U. S. Bur. Mines, Carnegie Inst. of Tech. and Mining and Metallurgical Advisory Boards (1930).

FeO)^3 = 5.7 × 10^{-7} at steelmaking temperatures. The amount of FeO in equilibrium with various amounts of aluminum in steel is shown in Table 1.

TABLE 1.—*FeO-Al Equilibrium in Steel*

Per Cent. Al	Per Cent. FeO	Equivalent Per Cent. Oxygen
0.5	0.013	0.0029
1.0	0.008	0.0018
1.5	0.006	0.0013
2.0	0.005	0.0011

If 1.0 per cent. Al is added to the steel, the amount of residual FeO will be very small, and may or may not be neglected according to the accuracy desired in making the determination.

The method proposed is deoxidation of the liquid steel with excess aluminum, determination of the Al$_2$O$_3$ formed, and conversion of this to its equivalent in FeO.

Sampling the Steel

A test-spoon is well slagged, and as soon as the steel sample is withdrawn from the furnace about 5 in. of ¼-in. aluminum wire is thrust into the steel. This amounts to about 1 per cent. Al in a 2½-lb. test. It is best to avoid putting the aluminum wire into any slag on the spoon, as this causes a decrease in efficiency of the aluminum addition. As soon as the aluminum has been added, the steel is poured into a small mold 1¾ in. square at the top, 1¼ in. square at the bottom, and 2½ in. deep (inside dimensions). It has been found advisable to use a sink head with this mold, and in Bureau of Mines practice the mold casting is simply made with a 2⅜-in. square section on top of the 1¾-in. square top of the mold; this section is 1 in. high and gives a sufficient amount of feeding to prevent piping in the small ingot. The test ingot is bored from the bottom with a ¾-in. drill and, as shown later, it has been found advisable to go well up into the test piece. Studies of segregation of Al$_2$O$_3$ in these small tests show that there is irregular distribution in the piece; therefore it is advisable to take as many drillings as possible to insure getting a representative sample.

An unkilled test is poured with each killed test and is used as a blank for the FeO estimation. By analyzing the unkilled test in the same manner as the killed test, the insoluble residue in the steel, together with the blank on the reagents, is obtained. In most work there is no need to run such a duplicate test on every sample. As a rule the blank is about 4 per cent. of the total alumina found in the killed test.

Various methods of adding the aluminum were carried out: (1) The aluminum was placed in the mold and the unkilled metal poured over it. This method gave erratic results, as the metal usually froze so rapidly that only part of the aluminum dissolved. (2) The aluminum rod was inserted into the stream of metal during pouring into the mold. In this test both cold and hot molds were used. A comparison of these methods with the method of killing in the spoon is given in Table 2.

TABLE 2.—*Methods of Adding Aluminum*

Method of Addition	Per Cent. Al_2O_3
Killed in spoon	0.094
Aluminum in stream pouring into red-hot mold	0.090
Aluminum in stream pouring into cold mold	0.077

The results indicated that the freezing of the steel in the mold was too fast to allow complete deoxidation, and the procedure adopted was to kill the steel in the test-spoon.

Segregation of Al_2O_3 in Test Piece

Two test ingots (described in the section on sampling) were split and drillings were taken at the top, middle and bottom of the ingot, after the hot top had been sawed off. Three samples were taken at each plane, at equal distances from one another, the center sample being at the center line of the ingot. Percentage values for Al_2O_3 were as shown in Table 3.

TABLE 3.—*Percentage Values for Al_2O_3*

Ingot A

Plane	Outside	Center	Outside
Top	0.144	0.080	0.097
Middle	0.108	0.083	0.170
Bottom	0.084	0.104	0.091

Ingot B

Plane	Outside	Center	Outside
Top	0.138	0.223	0.140
Middle	0.164	0.134	0.192
Bottom	0.184	0.144	0.158

On deep etching, the segregation was found to be very irregular, a condition always found in small ingots of aluminum-killed steel.[7]

[7] C. H. Herty, Jr., G. R. Fitterer and J. M. Byrns: *Op. cit.*

In view of the irregular segregation, the piece was drilled as described in the paragraph on sampling.

EFFECT OF EXCESS ALUMINUM ADDED

To determine whether complete deoxidation had occurred when the aluminum was added, also to obtain the effect of excess aluminum on the oxygen content of the steel, three series of tests were taken from a basic open-hearth heat, the first series at 0.50 per cent. carbon, and the second and third series at 0.10 per cent. carbon. Six samples were taken in each period. The aluminum was added as ¼-in. pure aluminum
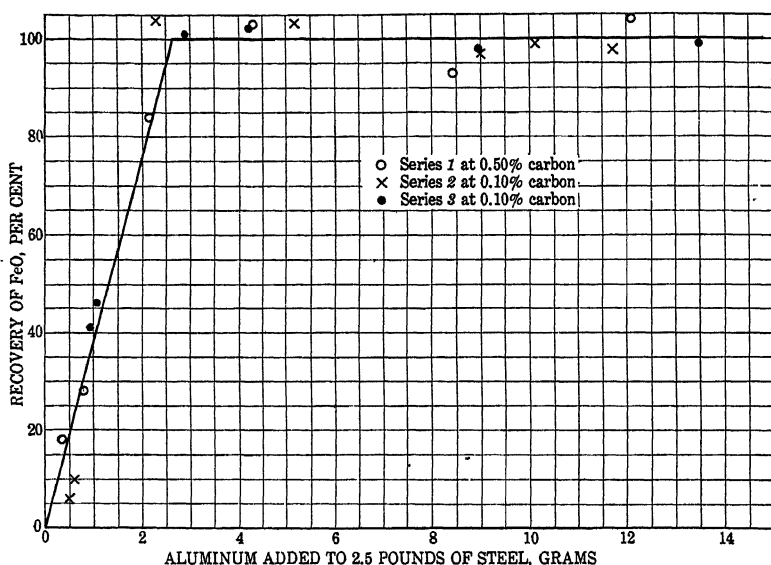
FIG. 1.—EFFECT OF EXCESS ALUMINUM ON DETERMINATION OF FeO IN STEEL.

wire, and the amount added was obtained by weighing the wire before and after use. Table 4 gives the results of these tests.

After a certain amount of aluminum had been added the amount of Al_2O_3 obtained was practically constant, and an average of the determinations giving approximately constant results was used to designate complete deoxidation. The percentage of FeO determined by various additions was then calculated by dividing the Al_2O_3 obtained on a given test by the average Al_2O_3 as shown above, and the results were plotted in Fig. 1. This figure shows that up to 2.5 g. of aluminum, the amount of FeO recovered was directly proportional to the aluminum added to a 2½-lb. test. After this amount had been added there was no increase in FeO content of the metal shown, indicating (1) that essentially complete deoxidation had been obtained, for if the rate of reaction between

added aluminum and the iron oxide was too slow to give the total amount there would be a gradual increase in Al_2O_3 content with increasing aluminum additions; and (2) that excess aluminum in the metal causes no increase in apparent oxygen content of the metal by deoxidizing the slag in the spoon or by atmospheric oxidation of the contained aluminum.

TABLE 4.—*Effect of Excess Aluminum Additions*

Carbon, Per Cent.	Aluminum Added		Al_2O_3 Found, Per Cent.
	Grams	Per Cent.	
0.50	None	None	0.0091
	0.35	0.042	0.0139
	0.80	0.079	0.0166
	2.15	0.33	0.0315
	4.30	0.40	0.0365
	8.45	0.79	0.0340
	12.10	1.12	0.0370
0.10	None	None	0.0100
	0.95	0.119	0.055
	1.05	0.218	0.060
	2.90	0.536	0.121
	4.20	0.583	0.122
	8.95	1.35	0.117
	13.5	1.35	0.118
0.10	None	*a*	0.0100
	0.50		0.0150
	0.60		0.0185
	2.25		0.0945
	5.15		0.094
	9.00		0.089
	11.70		0.090

a Tests on this series were not weighed.

As seen in Fig. 1, the results were consistent and indicate that the method is entirely satisfactory, provided an excess of aluminum is added.

EFFECT OF ALUMINUM ON OXIDES OTHER THAN FeO

If the metal has been deoxidized with silicon or manganese, almost all of the manganese oxide present, and part of the silica is reduced. Under these conditions the true FeO content of the steel is not determined, and work is being carried on at the present time on the percentage reduction of silica by aluminum.

ANALYTICAL METHOD FOR DETERMINATION OF Al_2O_3

Weigh out 20 g. of steel into an 800 c.c., or liter, beaker. Add 400 c.c. of distilled water. Set on hot plate until slightly warm and then

add 100 c.c. concentrated hydrochloric acid. Keep on hot plate or in warm place until action is complete. It is not necessary to boil the solution. Stirring or some agitation of the contents of the beaker, especially when finely divided carbon, etc. is inclined to form on the sides of the beaker above the solution, helps to bring into solution all the contents.

After the mixture has been allowed to stand several hours (preferably overnight) it is filtered through a retentive filter (Whatman No. 42). A careful inspection of the beaker at end of filtering is made, as small amounts of the residue are inclined to adhere. The filter is then washed with hot H_2O followed by hot 1:1 HCl; then two washings with hot water. These washings are carried out until 1:1 HCl acid is used four times, followed each time by two washings of hot H_2O.

The filter paper is placed in a weighed platinum crucible and dried on a hot plate. It is then placed in a muffle furnace until ashed to white or at least very light gray residue. If not of this appearance the residue is redissolved in 20 per cent. HCl, as used at first to get rid of iron.

To the residue in the platinum crucible about 5 c.c. of H_2F_2 and 5 drops of concentrated H_2SO_4 are added. The crucible and contents are placed on a hot plate until practically all of the dense SO_3 fumes have been driven off. The crucible is then placed in a hot muffle for about 5 minutes.

The crucible is placed in a desiccator, cooled and weighed. The increase in weight of the crucible originally weighed is Al_2O_3. The H_2F_2 treatment is repeated until constant weight is obtained.

The Al_2O_3 from the blank is subtracted from the total amount present and the percentage of FeO in the metal is calculated by multiplying the per cent. Al_2O_3 found by 2.11. This gives the percentage of FeO in the steel.

The Al_2O_3 residues have been converted to aluminum phosphate, and the amount of phosphate formed checked closely with its equivalent on the initial residue.

OPEN-HEARTH TESTS

After a number of determinations of FeO had been made on steels both in the laboratory and in the plant, it was decided to follow a complete heat, determining the FeO content of the metal from melt-down to tap, and to obtain as wide a range of iron-oxide content as possible. A basic and an acid heat were investigated. Both heats were charged to melt high in carbon and were worked down to about 0.10 per cent. carbon before tapping. On these two heats the main point at issue was to try the method for determining iron oxide rather than to attempt to obtain a steel low in iron oxide. Complete records on these two heats are not given in this paper because they will be parts of other papers.

PRELIMINARY STUDY OF A BASIC OPEN-HEARTH HEAT

Fig. 2 shows the results on a 50-ton basic open-hearth furnace.   In this figure are the FeO in the metal, carbon in the metal, FeO + Fe_2O_3
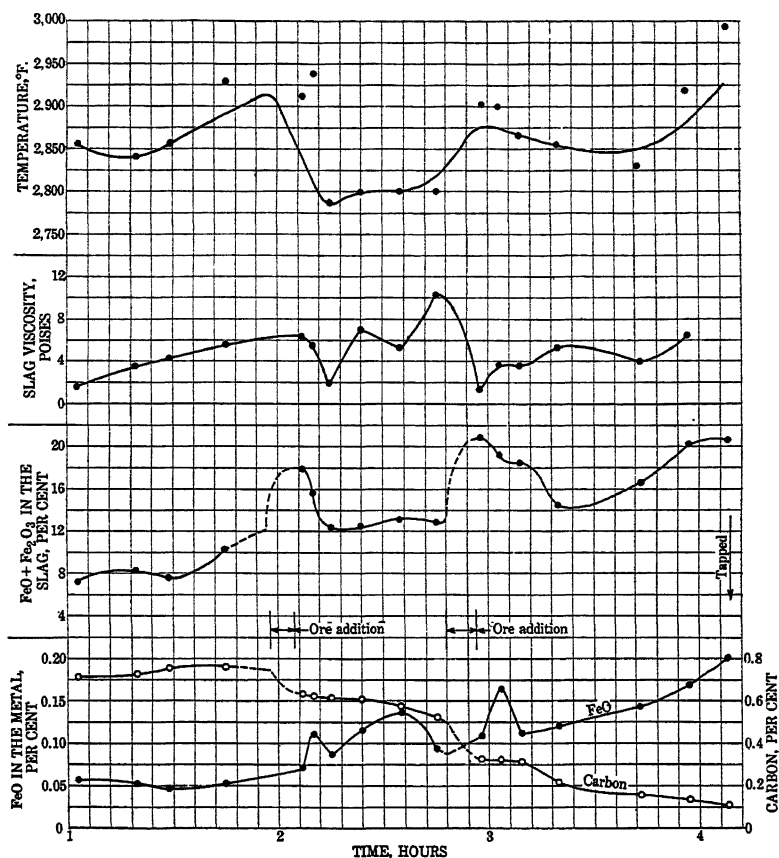
FIG. 2.—IRON OXIDE IN BASIC OPEN-HEARTH STEEL.

in the slag, slag viscosity as measured by the inclined plane method, and temperature as calculated from the manganese equilibrium constant. Table 5 gives analyses of the slag at melt-down and at tapping.

[8] C. H. Herty, Jr., C. F. Christopher and R. W. Stewart: The Physical Chemistry of Steel-making: Deoxidation with Silicon in the Basic Open Hearth Process. *Bull.* 38, U. S. Bur. Mines, Carnegie Inst. of Tech., and Mining and Metallurgical Advisory Boards (1930).

[9] C. H. Herty, Jr.: Chemical Equilibrium of Manganese, Carbon and Phosphorus in the Basic Open-hearth Process. *Trans.* A. I. M. E. (1926) **73**, 1107.

C. H. Herty, Jr. et al: The Physical Chemistry of Steel-Making: The Solubility of Iron Oxide in Iron. *Bull.* 34, U. S. Bur. Mines, Carnegie Institute of Technology, and Mining and Metallurgical Advisory Boards (1927).

TABLE 5.—*Analyses of Slags*

Constituent	At Melt-down, 1:45 p.m. Per Cent.	At Tap, 3:57 p.m. Per Cent.
FeO	7.79	15.93
Fe₂O₃	1.83	3.40
MnO	10.29	9.59
SiO₂	25.44	21.36
P₂O₅	1.05	2.23
CaO	39.65	33.03
MgO	11.30	9.54
Al₂O₃	2.32	4.10
Per cent. Mn in metal	0.37	0.20

Fig. 2 shows some interesting results: As the carbon was eliminated the FeO content of the metal gradually built up, the increase in FeO being rather rapid as the carbon approached 0.10 per cent. Following the ore additions the FeO content of the metal increased rapidly, but this increase did not come until about 6 min. after the end of the addition of ore, although the FeO in the slag was high immediately after the ore addition. The fact that the carbon content of the metal decreased considerably without any increase in iron oxide in the metal at the time of the ore addition indicates that the first action of the ore is similar to the action when the heat is rodded; that is, the boil occurring on the surface of the cold ore is sufficient to start carbon elimination, which proceeds rapidly enough to prevent a building up of iron oxide. As the ore begins to melt, the violence of the boil diminishes, carbon elimination slows up, and the iron oxide content of the metal increases. The fact that the iron oxide content of the metal drops sharply after the maximum is reached may be due to diffusion of FeO to the lower layers of metal, as carbon elimination was slow during this drop in FeO.

The curves of FeO in the slag and FeO in the metal are very similar, indicating the important part that oxidation of the slag plays in oxidation of the metal. An extremely interesting point in this connection is the period 2:36 to 2:48. With a slight increase in FeO in the slag, a marked decrease in FeO in the metal occurred with a similar decrease in carbon content in the metal. At this period the slag viscosity increased rapidly, and it is evident that the metal was being deoxidized by carbon faster than it was being oxidized by the slag, the increased slag viscosity slowing down the diffusion of FeO from slag to metal. Carbon elimination from 2:10 to 2:24 was very slow as a result of the low temperature at that time. The calculated bath temperature was 2785° to 2800° F., and the metal tests were sluggish when poured into the molds as a check on the calculated temperatures.

In general, therefore, the method of determining FeO in the metal gives results that check with theoretical and practical considerations on oxidation of the bath.

PRELIMINARY STUDY OF AN ACID OPEN-HEARTH HEAT

The results on the acid heat are shown in Fig. 3. The heat was intentionally melted high in carbon for comparison with the basic heat described in the previous section. The increasing oxidation of the
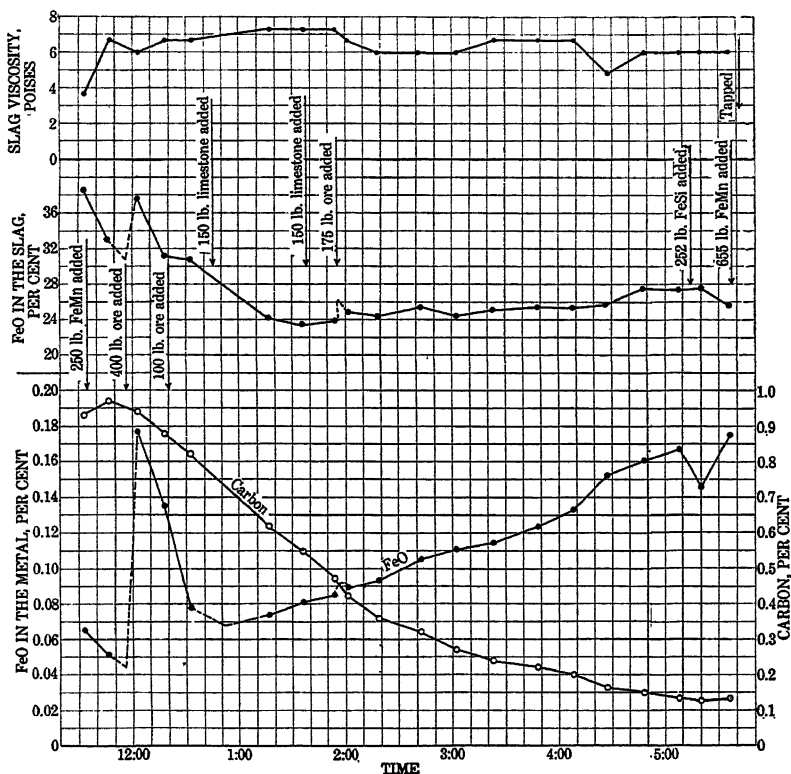
FIG. 3.—IRON OXIDE IN ACID OPEN-HEARTH STEEL.

metal as carbon is eliminated is strikingly shown in this figure. There was a rapid increase in oxidation after the first ore addition, and those following showed little if any effect, probably on account of the low percentage of iron oxide added; that is, 100 lb. of ore would have little effect on the slag as shown by the curve of FeO in the slag. At the ferrosilicon addition at 5:14, a drop in FeO occurred, but this drop should actually have been greater than shown on the figure. If the steel contains silica particles, a certain percentage reduction of SiO_2 occurs, thus making the observed FeO content of the metal greater than the actual content, as

was brought out earlier in this paper.   At 4:08 the slag thinned considerably, and there was an accompanying rise in FeO content of the metal with increased rate of carbon elimination at this time, showing the effect of slag viscosity on oxidation of the metal.   In this heat the aluminum method seems to give excellent results in determining the iron oxide content of the metal.

SUMMARY

A method of determining the iron oxide content of liquid steel has been described.   The method consists of adding aluminum to steel in a test-spoon, pouring the killed steel into a suitable mold, and analyzing the metal for Al_2O_3, from which the FeO in the steel may be calculated. From the experiments carried out to date the method gives every indication of being quantitative.   Results on a basic and an acid open-hearth heat have been included in this paper, but no attempt has been made to go into the theory of steel refining on the basis of these two heats, as the data will be used in conjunction with other heats for this purpose.   Some outstanding features, however, have been indicated.

DISCUSSION

[This discussion refers also to the paper by A. L. Feild, which begins on page 23.]

T. R. CUNNINGHAM, New York, N. Y.—Dr. Herty says that the Al_2O_3 is insoluble in acid.   The solubility of Al_2O_3 in hydrochloric acid, as we all know, depends upon the length of time subjected.   I am confident that if a steel containing finely divided Al_2O_3 is treated with warm 20 per cent. hydrochloric acid for as long a period as 18 to 20 hr. an appreciable amount of the Al_2O_3 present will be dissolved.   Check results do not mean anything, if made under the same conditions, as to strength of acid, temperature and time.   With Dr. Herty's permission, I wish to say that on a sample of steel he sent us last fall, which had been killed with aluminum-silicon, the Al_2O_3 inclusion contained considerable oxide of iron which could not be removed by treatment with hydrochloric acid.   The iron was believed to be tied up with the Al_2O_3 as ferrous aluminate.   If this aluminate is treated with hydrochloric and perchloric acids, and the solution evaporated to strong fumes of perchloric acid, the iron and Al_2O_3 are dissolved, leaving the silica.

C. H. HERTY, JR.—There is no question but that if you deoxidize a steel with a small excess of aluminum you will get alumina or ferrous aluminate, depending on the excess of aluminum added.   On the particular sample that Mr. Cunningham speaks

of, we had a very small excess of aluminum, about 0.05 per cent. In the experiments just cited, we had a considerable excess, about 1 per cent. aluminum in the steel. Under the microscope it is almost impossible to find anything but very finely dispersed alumina in the steel. Furthermore, when that is dissolved in 20 per cent. hydrochloric acid at a temperature of 50° C. and allowed to boil slowly in the solution, there is no trouble with iron in the residues.

If there were any appreciable amount of FeO tied up with the Al_2O_3 it certainly would appear where a weak hydrochloric acid is used. In other words, we have taken up residues and we always get between 96 and 98 per cent. Al_2O_3 in the residue and a small amount of iron.

T. R. CUNNINGHAM.—Suppose the steel contained considerable silicate; then there would be trouble again with the iron aluminate.

C. H. HERTY, JR.—As I pointed out, open-hearth steel before deoxidation contains a very small percentage of silica, as shown by an analysis for SiO_2 or total silicon. The amount is so small that it would not interfere with the results obtained by the method under discussion.

T. R. CUNNINGHAM.—In that case this method only actually determines the FeO in the steel.

C. H. HERTY, JR.—No. If you determine the silicates on an unkilled test taken simultaneously with the test, and then determine the silicates on the killed test, you have a measure of the amount of aluminum used up in deoxidizing those silicates. We have done that on two series of killed and unkilled tests and found 35 per cent. of the silica reduced and 65 to 70 per cent. of the ferrous silicate reduced. Subtracting gives the residual FeO, and it is remarkable the check that can be obtained on different samples.

We have tried it out on Bessemer steels and found that even after treatment with very strong acid, the silica cannot be gotten rid of unless the residue is fused.

R. O. GRIFFIS, Ashland, Ky.—How long does it take to make the determination?

C. H. HERTY, JR.—The way we run it is to start the determination late in the afternoon. Let the samples dissolve over night, and by morning they are well settled out so that a great deal of time can be saved in filtering. If the test is taken in a hurry probably it would take 2 or 3 hr., because the alumina is hard to filter. It must be allowed to settle. The test is speeded up considerably if it is started at night and finished the next morning.

A. B. KINZEL, New York, N. Y.—I have been much interested in the discussion we have just heard regarding the chemistry of this process. It seems to me almost obvious that the whole matter hinges on the degree of accuracy claimed for the test. Just what claims are made for accuracy?

I think Dr. Herty will agree readily that in most commercial open-hearth steel, a certain amount of silica and a certain amount of manganese from the initial charge, known as residual, comes right through. So even test samples taken before the steel is killed will have a certain amount of silica in them. There may be enough to give an error greater than the degree of accuracy claimed.

Moreover there is undoubtedly an equilibrium between iron, oxygen and aluminum. There is always some iron oxide left. The question is, how much?

It seems to me, from what we have heard so far, that the method is quantitative, as we would think of it in certain types of metallurgy, but not quantitative as the chemical analyst considers quantitative analysis. The method certainly is a useful tool which

should result in a worthy contribution to the study of the open hearth. I should like to see Dr. Herty use it in such a study.

C. H. HERTY, JR.—Table 1 gives the percentage of FeO left. It is determined by Mr. Fitterer in his work at the Bureau of Mines.

The paper was intended simply to give the method and what work we had done at the time. As I have said, since then we have done enough work not only to feel that we are beginning to get a useful tool, but also that it is almost quantitative in its correlation with other qualities in the open-hearth furnace. The question as to the silica present has already been answered.

A. L. FEILD, Lockport, N. Y.—It seems to me that the criticism, if it can be called criticism, directed against Dr. Herty's method is not entirely justified. I do not believe he claims the method to be quantitative in the sense of a chemical analysis, but when we remember that there is no other method that comes anywhere near giving FeO, it seems to me it represents a decided advance.

Also, as the speaker probably neglected to point out, in most cases where he takes samples from the metal bath the method shows so much iron oxide that practically all the silica has been fluxed out, and the only question that remains is how much manganese oxide there is dissolved. My own opinion is that aluminum would reduce this oxide. In other words, it is one thing to talk about what obtains for "killed" steel, and it is another thing to talk about what holds for steel in the open hearth, especially before deoxidation.

I do not see why there need be any fear concerning silica if the sample is taken before deoxidation. When, for example, Dr. Herty finds approximately 1 per cent. FeO in his open-hearth sample, the effect of a few hundredths per cent. oxygen, which may be present as MnO, or as SiO_2, does not seem to me to be important enough to affect the practical value of this test. So far, I have not heard a better test proposed.

L. F. REINARTZ, Middletown, Ohio.—We have been much interested in the work that Dr. Herty and Mr. Feild have been doing on the oxidation of steel, but Mr. Feild's first two papers were a little above my head. I have forgotten much of my differential calculus. The discussions today have made it clearer, and we can see some relationship between the practical and the theoretical work.

For many years in our practice in steelmaking, we have been controlling analyses and refining operations by iron oxide determinations in the slag. For that reason, we have always been interested in having some method developed whereby the iron oxide could be determined directly in the metal itself.

Mr. Feild talked about the rate of iron oxide production compared with the carbon elimination, and in practical operation that relationship must be known in the different grades of steel that are being made. If a high-carbon steel is being made in which the iron oxide should be very low, it is necessary to come down under a very quiet bath. There must not be a great deal of action in the bath. However, from a commercial standpoint, if you want to get down to 0.08 per cent. carbon, you want to get iron oxide in the bath in order to speed up the reaction as rapidly as possible. If there is a rapid carbon drop it will be detrimental to the finished heat, for there may be an off-grade heat or the steel may be overoxidized and will not serve the purpose intended, because, in order to neutralize the iron oxide too much oxidizer has had to be added. In the lower carbon ranges, the proposition is different because you expect to finish with a considerable amount of iron oxide in the slag and in the metal.

Mr. Feild brought out the point that stirring the bath will not reduce iron oxide. We can support him in that statement. We stir the bath with saplings and with steel poles in order to create a boil. We do not decrease the iron oxide; if anything,

we increase it. But we do decrease the carbon and it speeds up our work from that standpoint.

When Dr. Herty sent me this last paper we immediately made an arrangement to try out the test. Our metallurgist took about 5-lb. samples from the furnace. When we tried to deoxidize the metal with the aluminum, we first poured the metal from the spoon into a test box and deoxidized it in the test box. There a certain amount of boiling went on in the spoon and our results were low on the iron oxide. We then followed the method that Dr. Herty recommended, exactly or as nearly as we could. We deoxidized with a ¼-in. aluminum rod directly in the spoon as soon as we could after it was taken out of the furnace. We did that on two heats, using 7½ g. of aluminum on each 4-lb. sample, which corresponds closely with the recommendation Dr. Herty made.

We were rather disappointed in one thing, and that is the length of time it took to run the determination. It took us about 8 hr. to run the test. We made a check test on each of two heats. (The chemists later on said they believed the determination could be done in 2½ hr., which also checks with Dr. Herty's statement if all conditions are right.)

We were highly pleased and delighted to find that on the one heat the two tests taken within 2 or 3 min. of each other checked within the limits of chemical error in a commercial laboratory. In other words, they checked within about 1 per cent., which would be close enough for any commercial work. The second heat had about the same iron oxide in the slag as the first and checked the first heat practically within the limits of chemical error on the iron oxide. We were much pleased at that. It showed that those two heats were practically in equilibrium as far as the slag and the metal were concerned.

The second test of the second heat boiled a little in the spoon before we were able to deoxidize it completely, so the percentage of alumina that was recovered was about 15 per cent. low.

But to us it looks as though this method were going to be entirely practical from the standpoint of research work. Unless you can run it much faster than we so far know it can be run, it will not be of much value as a control medium. But from the standpoint of following the reactions that take place in the bath, and in controlling the quality of the metal, there is no question in my mind that we are going to get good results from these methods.

T. D. YENSEN, East Pittsburgh, Pa.—The discussion so far has been largely in connection with Dr. Herty's paper. I should like to point out an obvious conclusion in connection with Mr. Feild's paper: The fact that it is impossible, in an ordinary open-hearth furnace, to obtain a carbon content less than 0.02 per cent. shows that it will be necessary, in order to get lower carbon and oxygen contents, to employ some different method.

Most of you are familiar with the fact that in Germany furnaces of the vacuum type have been developed on a commercial scale. I have heard of furnaces of 4, 5 and 6 tons capacity. However, it is not sufficient, according to Mr. Feild's paper, to employ a vacuum without at the same time producing a violent stirring of the bath, because of the fact that the carbon monoxide pressure in the lower part of the bath will be sufficient to maintain a carbon and oxygen content of large proportions. In other words, in order to obtain low carbon and oxygen it will be necessary to employ a vacuum *and* a violent stirring, and perhaps the only method of doing this will be by means of the high-frequency or the low-frequency induction type of furnace.

A. B. KINZEL.—I want to be sure that Dr. Herty understands that my discussion was in no way an adverse criticism of what he has done. I was simply pointing out

that it is a metallurgical tool and a very good one.   There is no question about that whatever.   I agree with Mr. Feild entirely in that.

Regarding Mr. Feild's paper, the matter of equilibrium at the end of the boil is of great interest.   When an ordinary chemical reaction is started, it generally goes to equilibrium without stopping, unless some strenuous force is applied in some way, or some other factor develops.   In an open hearth, there is a boil which stops before it comes to equilibrium if we assume one atmosphere CO pressure during the boil.   Then why does the boil stop?   This is, in a sense, a rhetorical question; that is, we do not know the answer, but it is something we want to think about.   We at the Union Carbide Research Laboratories, particularly since we determined the low value for the equilibrium constant, have given it much thought.   We certainly hope that other metallurgists will give this further consideration.

A. L. FEILD.—Mr. Kinzel's question of why the carbon boil stops is a hard one.   We know, though, that as carbon drops the total amount of gas coming out gets smaller.   The number of places where the bath is broken becomes smaller.   There finally comes a time when, due to the decreased volume of CO, it simply stops.   It finally simmers down to where it cannot form bubbles in the metal.

I think Dr. Herty, or someone, spoke about the high pressure required to form a bubble.   The bubble forms to carry away the excess pressure of dissolved CO.   There will come a time when the bath gets overheated with respect to CO, as a kettle of water does with respect to water vapor.   That probably happens gradually rather than at any sudden moment.

C. H. HERTY, JR.—I should like to talk about the low pressure.   I will use Mr. Feild's equation:

$$-\frac{dx}{dt} = k(xy - mP)$$

In the boil there is a pressure of one atmosphere of CO.   Therefore $P = 1$.   According to Kinzel, m would be 0.0005, and you would expect the rate of carbon drop to be in proportion to $xy - 0.0005$.   On the other hand, we find that the rate of carbon drop is proportional to $xy - 0.01$ at about 1600° C.   The value 0.01 was obtained by plotting the rate of carbon drop against the product (C)(FeO), the FeO being determined by the method described in this paper.   Many tests were made, and the experimental points fell in a very good line, the line intersecting the (C)(FeO) axis at (C)(FeO) = 0.01.   From these data we have calculated also the rate constants for the carbon-iron oxide reaction and find that they come out very uniformly.   The reason the bath stops boiling is that as soon as the concentration of carbon and iron oxide satisfy the expression (C)(FeO) = 0.01 the reaction is at equilibrium, so that no bubbles of gas would be formed.

We have one heat which brings out just what Mr. Feild was talking about.   The carbon was dropping after a reboil with silicon from 0.12 to about 0.07 per cent. carbon and we intended to take the heat out at 0.07 carbon.   But unfortunately, or fortunately for us, a delay in the pouring of another heat prevented tapping and we had a heat that lay dead in the furnace for 1 hr. 15 min.   At 4 o'clock the carbon was 0.046, and at 5:15 it was 0.042.   In other words, the amount of carbon eliminated was so small that it was almost zero within the limits of accuracy.   When the boil stopped, the value of m was 0.013.   During the next 1¼ hr. the value of m gradually picked up to 0.017.

L. F. REINARTZ.—I think the point that everybody must realize is that a great many factors have not been considered in the drop in the carbon in a bath of steel. In the particular illustration given, a great deal depended on the first helper—how he

held the heat and how he held the slag. You can make a heat go dead by changing the viscosity of the slag. When the metal is high in carbon a large accumulation of carbon monoxide builds up under the slag.

H. STYRI, Philadelphia, Pa.—I am coming back to Feild's equation, No. 7 in his first paper,[10] which Feild has credited me with being the only one not willing to accept while he has claimed it generally approved, generally in this case meaning Mr. Kinzel and Mr. Piérard. I have previously twice stated reasons why I consider his equation No. 7 wrong and shall now for a third time try, by using some simple mathematical analogy, to show why he is wrong.

Let us consider two curves in one plane (Fig. 4), curve a representing the carbon-time curve in the open system where oxygen has access to the bath and curve b the carbon-time curve in the closed system of steel below the slag-metal interface, with no supply of oxygen or carbon from outside sources.
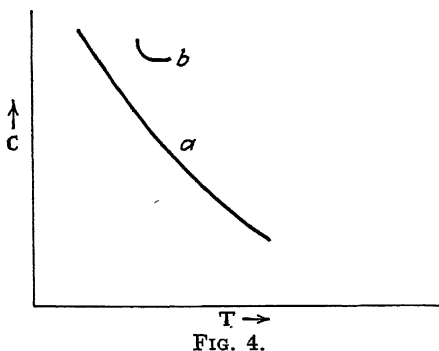
FIG. 4.

To illustrate Mr. Feild's mathematical method in studying the combination of two such curves, I shall use a simple numerical example from sophomore mathematics, which used to amuse me some 25 years ago, and for that purpose select the following arbitrary equations:

$$y^2 + 2y + 3 = X \text{ and} \qquad [1]$$
$$y^2 + 3y + 4 = X \qquad [2]$$

which you will recognize as two parabolas with the axis parallel the X axis. Differentiating, we get

$$\frac{dy}{dx} = \frac{1}{2y + 2} \quad \text{and} \quad \frac{dy}{dx} = \frac{1}{2y + 3}$$

If we apply Mr. Feild's method and introduce the value of dy/dx from equation 1 into equation 2 we get

$$2y + 3 = 2y + 2$$

or

$$3 = 2$$

which obviously is wrong; and it is wrong because the two values of y in the two equations are not the same for the contact points of the tangents of the two curves which have the same slope.

If we remember this and give suitable subscripts to the variables, we can determine the corresponding points of the curves which have parallel tangents. In this example we get

$$y_1 = \frac{2y_2 + 1}{2}$$

[10] Iron and Steel Technology in 1928, A. I. M. E. (1928) 122.

representing the relation between ordinates for the two curves having the same slope of the tangents.

This illustrates my reason for saying that Mr. Feild's equation 7 is wrong.

The curve representing the reaction in the closed system is drawn with considerable change in curvature but with little total drop in carbon because, as may be taken from Dr. Herty's data, the amount of oxygen available for elimination of carbon corresponds only to about 0.01 per cent. carbon. The change in curvature must be rapid because any elimination of carbon must rapidly reduce the oxygen and thereby the velocity of the reaction. The reaction in the steel bath under the slag is therefore absolutely dependent on outside variations and the reaction velocity in the closed system must run parallel with the reaction velocity in the open system. It simply means that the reaction in the closed system must keep step with that in the open. The carbon cannot go any faster or slower than oxygen is supplied from the outside, and the reaction velocity consequently is controlled by the rate of diffusion of oxygen into the bath.

A. L. FEILD.—Dr. Styri has explained his ideas several times in different ways. We have never agreed on the points involved and the possibility of agreement would appear to remain remote. He has arbitrarily selected two equations here to correspond to my two equations. One of my equations represents the law of conservation of matter. It is universally true. The other is the equation of mass action. They are both true independently of each other. Mr. Styri cannot say that his two equations are true independently of each other, because they are obviously inconsistent and present no analogy to mine.

Practical Observations on Manufacture of Basic Open-hearth, High-carbon Killed Steel

By W. J. Reagan,* Oakmont, Pa.

The problem of increasing output and decreasing percentage of rejections is a vital one in the manufacture of steel of any kind. The making of basic open-hearth steel for use in rolled steel wheels, tires for locomotive and car wheels, and forgings of various kinds, is a highly specialized industry. The increase in weight of railway rolling stock of all kinds, and the high speed that the public demands of transportation facilities, make it imperative that steel for use in this class of material shall be of the highest quality obtainable.

During the past few years it has been the writer's good fortune to have opportunity to study the defects in basic open-hearth steel, and also the results obtained by various changes in open-hearth practice, on such defects. The opportunity for study and the details available are rarely found in the manufacture of steel of any kind. It seems reasonable to assume that many of the results determined here can be applied to the production of steel of other types with a decided improvement in quality, a decrease in the percentage of rejections and an increase in output.

All of the material described is basic open-hearth steel with the following range of analysis: carbon, 0.50 to 0.85 per cent.; phosphorus and sulfur, 0.04 max.; silicon, 0.15 to 0.35; manganese, 0.50 to 0.75.

All of this material is bottom-cast, therefore tapping and pouring temperatures are higher than in top-cast production.

Ingots used in this type of work are of standard length with varying diameters. The ingot is known as duodecagonal, or twelve-sided. The standard body length is 88 in. and the hot top length, 14 in. Fig. 1 shows a typical ingot of this type. The diameter varies from 13 to 30 in. Ingots for special forgings, which cannot be made in molds of standard size, are made in molds of various sizes and designs. These ingots are sliced cold, into blocks of various lengths, depending upon the weight of the forging to be made. Fig. 2 shows the ingot after coming from the slicing lathe. Just sufficient metal remains between blocks to hold the ingot in one piece while it is being removed from the lathe; then steel wedges are inserted between the blocks and the blocks are broken apart. This affords abundant opportunity for inspection, as the interior of the

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* Open Hearth Dept., Edgewater Steel Co.

ingot from top to bottom and from outside to the very center is open to view.

The blocks are numbered with heat number, ingot number and block letter as soon as the ingot is split. The heat number and ingot number indicate the time of making and the position in which it was cast, either in a group of eight or singly, and from which ladle. The block letter gives the location of the block in the ingot, all bottom blocks being identified with the letter A. All of this information, together with other details of its history, such as reason for rejection, etc., is entered on a card, which is punched with holes in various sections, to be used in an automatic tabulating machine. Each card contains the complete history of one block, thus it is possible to assemble any desired information, and by any desired grouping in the tabulating machine to obtain practically any information desired.

All heats are tapped into two ladles, through a bifurcated spout, which gives additional opportunity for studying changes in practice, variations in pouring speed, and so forth.

Fig. 1.   Fig. 2.

Fig. 1.—Duodecagonal ingot.

Fig. 2.—Ingot sliced into blocks.

RAW MATERIALS

One of the most important considerations in the making of high-quality basic open-hearth steel is the selection of raw materials. Of these, perhaps the most important is basic pig iron. The desired analysis should show a silicon content of from 1 to 1.30 per cent., manganese at least 2 per cent., and higher if possible. Phosphorus under 0.20 and sulfur under 0.05 per cent. are desirable. Phosphorus up to 0.30 can be handled without much difficulty.

High manganese is desirable for several reasons; primarily to give a high residual manganese in the bath at melting, with a corresponding saving in manganese in the final additions. High-manganese pig iron increases the fluidity of basic slags and also increases the manganese oxide in the slag, which leads to a decrease in silicates or nonmetallic inclusions in the bath.[1] High-silicon pig iron is desirable because it causes a heat to melt higher in carbon than when low-silicon pig is used. Thus for a given charge a considerable saving in pig iron is accomplished by using a high-silicon pig. High silicon also increases the temperature of the bath and tends to offset the loss of heat due to carbon elimination. Low-silicon iron, because of its lack of heat producing action, tends to
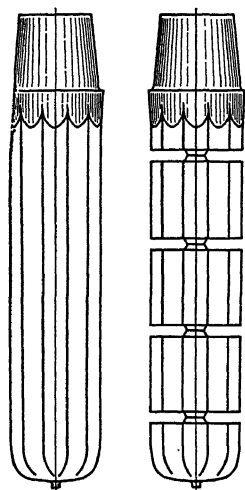
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[1] C. H. Herty, Jr.: Open-hearth Operation from the Chemical Viewpoint. *Trans.* A. I. M. E., Iron and Steel Div. (1929) 260.

give heavy viscous slags, which require additions of large quantities of fluorspar to thin them.   It is important that the analysis of basic pig iron should be constant.   A uniform analysis ensures uniformity in open-hearth operation and prevents the use of excessive amounts of iron ore on heats that melt too high; it also ensures freedom from heats that melt too low and require the use of no iron ore.   Pig iron of uniform analysis shows that the blast furnace supplying it is running steadily, and such regularity tends to keep the silicates low.[2]

Another raw material ·little considered is limestone.   Some time ago the U. S. Bureau of Mines issued *Circular* 6041 giving some interesting figures on the value of limestone.   The formulas given show the available carbonates in the stone; that is, the percentage of calcium and magnesium carbonates available for fluxing, after a sufficient percentage has been deducted to neutralize the impurities in the stone itself.   The open-hearth formula is $100 - 5.5 \times A$, in which A equals the percentage of alumina plus silica in the stone.   This also emphasizes the fact that magnesia has a lower affinity for phosphorus than calcium, therefore low-magnesia limestone is desirable.   High-magnesia limestone also produces a viscous slag during the working period, which is an undesirable condition in any practice.   Limestone of good quality should show the following average analysis: SiO_2, 0.40 per cent.; Fe_2O_3 and Al_2O_3, 0.60; $CaCO_3$, 98.74; $MgCO_3$, 0.20.

Another essential raw material is scrap.   Heavy melting scrap for basic furnaces should be free from all small sections, with their high oxidation loss, and alloy steel of any kind.   It should not contain scrap with large quantities of rust adhering.   The amount of iron oxide in the bath of an open-hearth heat depends upon the amount of iron oxide added in the charge, although other causes contribute their share.   Protected storage for raw material prevents rusting of works scrap and contributes materially to the reduction of iron oxide in the charge.

Raw materials with a uniform analysis and of high quality are important in the making of high-quality basic open-hearth steel.   The selection of the proper type of furnace also is important.   High tonnage and quality rarely are found in combination in forging steel.   An open-hearth furnace working too sharp makes cheap steel but not good steel; one working too slowly is just as much at fault, working of the steel too cold showing a high percentage of rejections.

DESIGN OF INGOT MOLD

Of all the factors exerting an influence on the kind of ingot produced, perhaps the most important is the ingot mold.   The influence of the mold

[2] C. H. Herty, Jr. and J. M. Gaines, Jr.: Unreduced Oxides in Pig Iron and Their Elimination in the Basic Open-hearth Furnace. *Trans.* A. I. M. E., Iron and Steel Div. (1929) 179.

on ingot structure, segregation, etc., is most important. For each kind of steel there is a design of ingot mold most suited to its purpose. The shape of the ingot, its taper, diameter, length, proportion of wall thickness to ingot body, etc., are all important. Our English friends, in their Report on the Heterogeneity of Steel Ingots,[3] have taken a big step forward towards eliminating some of the questions of ingot-mold design. It behooves every steelmaker to read this work carefully.

A troublesome source of rejections in ingots—cracks—has been found to be due to the design of the ingot molds. A mold with a wall section that is too heavy, especially for ingots of small diameter, is a producer of ingots with circumferential cracks close to the hot top. Ingot molds with a wall section that is too heavy tend to solidify the metal too quickly and to force the steel pourer to speed up his rate of pouring, to avoid the possibility of freezing of small sections of the metal before the entire ingot is cast. Heavy wall sections have a pronounced influence on mold life and it is possible to design molds that will have too long a life. Too long a life gives a poor ingot surface and provides a source of small hangers, which tend to produce cracks in the ingot surface.

We have found that the interior of the mold, instead of growing larger, as is generally supposed, actually grows smaller. This decrease in size is about in proportion to the mold life. Some molds have been found that were about $\frac{1}{4}$ in. smaller in diameter than when they were first placed in service. W. E. Remmers[4] gives a timely explanation of this phenomenon. He explains the growth of cast iron as precipitation, solution and reprecipitation of graphite in the solid matrix material. In the making of rolled steel car wheels it is important that the ingot diameter shall remain as nearly constant as possible, in order to give a supply of blocks of which the weight shall vary only slightly. Ingot molds made from cupola iron are more accurate as to inside dimensions than molds made from direct metal, but direct metal molds have a somewhat longer life.

The type of mold and runner in use in our practice is shown in Fig. 5. This mold has a rather heavy band around the top. This is to prevent cracks in the ingot-mold wall, and the fact that molds are never scrapped because of cracked wall sections is proof of its effectiveness. Another small but effective change in design is the gradual taper of the flutes to a perfect circle at the open end of the mold. This change has a marked effect on reduction of cracks in the ingot and gives a noticeable increase in ingot-mold life.

[3] Report on the Heterogeneity of Steel Ingots. *Jnl.* Iron and Steel Inst. (1926) **113**, 39; (1928) **117**, 401; (1929) **119**, 305.

[4] W. E. Remmers: The Permanent Growth of Gray Cast Iron. A. I. M. E. *Tech. Pub.* 337 (1930).

The question of mold wash is one that has been the subject of much controversy. Some time ago it was supposed that a wash of any kind applied to the interior of the ingot mold was a possible source, rather than a preventative, of contamination. Accordingly a test was run on about 200 heats to determine just what effect mold wash had upon the ingot and upon the ingot mold. On one ladle the molds were sprayed, as usual, with a tar wash; the other ladle of steel was poured into molds without a wash of any kind. Upon completion of the tests the results were tabulated, and the final figures caused considerable surprise. The percentages of rejections on both ladles were almost identical, with the exception of cracked ingots (circumferential crack from 2 to 3 in. below the hot top). The final results showed that from the ladle without mold wash the rejections totaled 3.29 per cent. for cracks[5] while from the ladle sprayed with tar the rejections formed only 1.13 per cent. for cracks.[5] These figures show without any question that an ingot-mold wash prevents cracks by providing lubrication of the mold wall. The effect of the mold wash upon the surface of the ingot mold cannot be determined accurately, but it is supposed that it materially assists in increasing the mold life. The wash in use at present is a graphite mixture, which is atomized and sprayed on the interior of the ingot mold with a high-pressure spray gun.

High manganese, about 1.5 per cent., and low phosphorous and sulfur are desirable qualities in ingot molds. High manganese, particularly, seems helpful to long mold life. An average life of 200 heats per mold is obtained from molds of this type, and it is not at all unusual to find molds with a life of 300 heats.

LADLES

Ladles lined with "circle" brick, laid so that there is no overhanging ledge, show a considerable increase in ladle life and less erosion from ladle slags. These bricks are laid with the 2½-in. width parallel to the shell of the ladle, which makes the interior of the ladle a smooth surface with the minimum amount of brick surface exposed to the steel. The usual custom when testing stoppers for leakage, when the stopper is being set, is to scatter a handful of sand around the stopper head, sometimes several handfuls. This sand shows up on the bottom surface of the ingots and sometimes is very noticeable. Powdered burnt lime can be used for this purpose and does not show up on the ingots, giving a much cleaner ingot surface.

OPEN-HEARTH PRACTICE

The old saying that "steel should be made in the furnace" is very true. The charge of raw material for an 80-ton basic open-hearth furnace making forging steel containing 0.75 to 0.80 per cent. carbon should be such that at melting the initial carbon will be sufficiently high to allow

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[5] This figure refers to pieces—which is also the approximate weight.

for a moderate addition of iron ore, and to have about two hours duration between this ore addition and the addition of the final deoxidizers. This enables the melter to shape up his slag in preparation for deoxidation, and also to slow down the rate of carbon elimination. Table 1 gives the charge of raw material on a typical heat of forging steel; also the analyses of the first steel test and a typical slag analysis.

Slag samples taken at this time show a test free from porosity and with a variety of color, depending upon temperature and SiO_2 content. A low-temperature slag appears as a gray black with a metallic appearance. A slag sample for viscosity taken by means of the inclined plane shows a heavy viscous slag. The inclined-plane method, developed by the U. S. Bureau of Mines, uses a section of $\frac{1}{4}$-in. plate, bent at an angle of 30°. The slag sample is taken in a spoon, well slagged, filled with slag, removed from the furnace and immediately poured down the inclined plane. The thickness of the slag layer on the plane at a distance 1 ft. from the top is taken as a measure of its viscosity.

Shortly after the first melting test, sufficient iron ore is added at one time to reduce the carbon to the required amount. About 3000 lb. of ore is the usual addition. After this addition, sufficient fluorspar is added to thin the slag to the desired viscosity, as determined by samples taken on the inclined plane. In an average heat of 0.75 to 0.80 per cent. carbon steel the carbon is allowed to drop to about 0.78 per cent. carbon, depending upon the temperature of the bath, condition of the slag, and the speed at which the carbon is dropping. Table 1 shows a typical steel and slag analysis at this stage, just before the addition of the deoxidizer. A slag viscosity test at this time will show a viscosity of from 0.10 to 0.12 in. and a slag cake for porosity should show a solid cake quite free from porosity. The slag cake is taken in a metal mold about $\frac{5}{8}$ in. deep and 3 in. in diameter.

At this time in a normal heat 1500 lb. of spiegeleisen is added. This material will average about 20 per cent. manganese and 2 to 3 per cent. silicon. This addition should kill all action on the bath. When it is added, the gas and air are cut down, which thickens the slag considerably. About 1500 lb. of burnt lime added at this time is also often desirable. This gives an added viscosity to the slag and enables the melter to finish the reboil with a thick creamy slag, which indicates a good condition of the heat after the reboil. Usually about 35 min. is required for the bath to come back on a good reboil, then the final addition of ferromanganese is made, all being added to the furnace. About 10 min. after the manganese addition, the heat is ready to tap. The final silicon addition is made in the ladle. A pick-up of carbon and manganese, sometimes as much as 15 points of manganese from the spiegel addition, denotes a complete degree of deoxidation. The final steel and slag analysis should be approximately as given in Table 1.

TABLE 1.—*Typical Heat of Forging Steel*

Charge, Lb.		Steel Analysis, Per Cent.				Slag Analysis, Per Cent.		
		First Test at Melting	Just Before Addition of De-oxidizer	Final Test	.	First Test at Melting	Just Before Addition of De-oxidizer	Final Test
Basic pig iron (50	C...	1.40	0.78	0.78	FeO...	4.50	7.50	7.63
per cent.), 87,000.	Mn	0.50	0.50	0.70	Fe$_2$O$_3$..	5.70	5.60	4.81
Scrap (50 per cent.),	P...	0.06	0.015	0.015	MnO..	17.60	11.00	12.39
87,000.	S...	0.03	0.02	0.02	SiO$_2$...	25.80	15.00	16.80
	Si..	Tr.	0.008	0.23	P$_2$O$_5$...	2.60	2.60	1.73
Limestone (10 per					CaO...	37.70	51.10	49.50
cent.), 17,500.					MgO..	5.50	4.34	5.21
					Al$_2$O$_3$..	1.80	2.00	

In view of the fact that so much important work on deoxidizers, etc. is being done by Dr. C. H. Herty and associates of the U. S. Bureau of Mines, it would be futile to try to discuss this problem here. However, we have found in our practice that spiegeleisen gives the best results of any deoxidizer used. The slags are better, the saving in manganese is considerable, and the conditions of furnace practice are generally better. On a number of heats deoxidized with spiegeleisen and 16 per cent. ferrosilicon pig, fewer nonmetallic inclusions were found on the spiegel heats than on the ferrosilicon heats. Also, the heats made with spiegel had the lowest percentage of rejections; in fact, the heat with the lowest percentage of inclusions ever analyzed proved to be 100 per cent. good; that is, there were no rejections of any kind for open-hearth defects. Much remains to be learned about the effect of deoxidizers, and present indications are that such information will be available in the near future.

An interesting study of approximately 100 heats of basic open-hearth steel has been completed recently. The most important results have been plotted on the chart shown in Fig. 3. On all heats, slag samples were taken for viscosity and porosity, together with tests killed with aluminum for dissolved iron oxide in the steel.[6] In addition, the slag temperature, residual manganese, rate of carbon drop, manganese oxide in slag, iron oxide in slag, carbon content and time charge to tap were plotted. All of these figures were taken just before the addition of the deoxidizer, except the time charge to tap.

The results show plainly the upward trend of dissolved iron oxide in the steel as the temperature of the bath decreases. It also shows exceptionally well the effect of temperature on the residual manganese

[6] C. H. Herty, Jr., J. M. Gaines, Jr., H. Freeman and M. W. Lightner: A New Method for Determining Iron Oxide in Liquid Steel. See page 28.
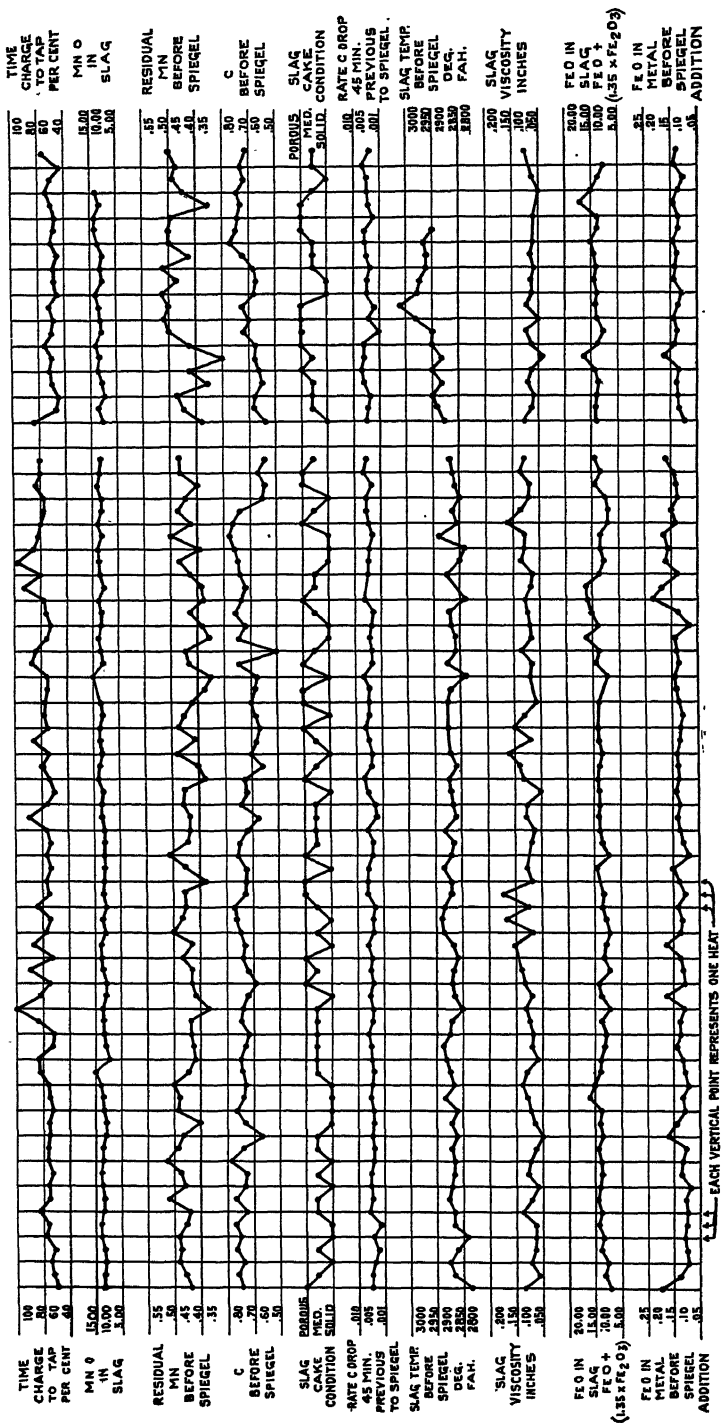
FIG. 3.—STUDY OF APPROXIMATELY 100 HEATS OF BASIC OPEN-HEARTH STEEL.

in the bath. The increase in residual manganese with the increase in slag temperature is very strikingly shown. The thinner slag viscosity with the higher slag temperatures is plainly shown; also, the increase of iron oxide in the steel with increase of the iron oxide in the slag. The upward trend of manganese oxide in the slag is indicated, following the higher residual manganese in the bath. The effects of increasing amounts of dissolved iron oxide in the steel are under investigation, but it can be stated now that heats with a high percentage of dissolved FeO show a correspondingly high percentage of rejections.

In connection with this study it has been found that temperature is the most important factor in producing variations in color, etc. in slag samples taken from high-carbon basic open-hearth heats. A heavy slag with a glossy black color and a creamy consistency is an indication of low temperature. Slags poured hot and fast show colors of green and greenish blue. It is difficult to determine FeO content, MnO content, etc. by visual inspection of slag samples.

Heats that melt at about 1.30 per cent. of carbon give the lowest percentage of rejections. This percentage of carbon enables an addition of a moderate amount of ore, contrary to some theories that it is poor metallurgical practice to have heats melt high enough to have to feed ore, and confirming the statement made by Radclyffe Furness, while in Pittsburgh some time ago, that he "likes to use a little ore."

Heats that melt too low, and without any ore addition, usually are producers of an abnormal percentage of rejections. No doubt these heats would show a high percentage of nonmetallic inclusions due to the inefficient action of deoxidizers on such a heat. On the contrary, heats melting too high, necessitating large amounts of ore to reduce the carbon, are also producers of abnormal percentages of rejections. Too much ore and too little ore tie up with heats that are too hot or too cold. Soaker heats should never be allowed. Heats that melt too low, and to which pig iron is added, should be handled with the greatest of care and all possible attention given the final deoxidation, to prevent a high percentage of rejections.

The use of aluminum in any form should be prohibited in the making of forging steel. A recent U. S. Bureau of Mines *Bulletin* (No. 46) goes into detail on the effect of aluminum in steel.

POURING PRACTICE

After the steel leaves the furnace and is ready to be poured into ingots, the troubles of the steelmaker are by no means over; in fact, they have just begun. Steel made with all possible care in the open hearth can be ruined by improper pouring practice. The results of such improper pouring are especially noticeable to the maker of bottom-cast ingots.

He must tread a straight and narrow path to keep his percentage of rejections down to normal. Temperature readings of slag in the furnace should be taken at frequent intervals by means of the optical pyrometer. Temperature readings at tapping and pouring are also essential; they enable the steel pourer to judge the pouring speed.

After the steel is tapped, it should be held in the ladle at least 10 or 15 min., depending upon temperature. This interval between tapping and pouring allows the inclusions which have been fluxed by the final deoxidizer to rise to the surface of the metal before pouring. Pouring speed should be governed also by the size of the ingot and by the condition of the ingot mold into which the metal is poured.

From observations taken over a considerable period of time, comparing variations of pouring speed on steel from two ladles from the same heat, it has been found that a high rate of pouring speed gives a consistent production of ingots with circumferential cracks on the ingot surface, within a few inches of the hot top. Other reasons for cracked ingots are pouring metal into cold molds, lack of mold wash, bad surface conditions on the interior of the ingot mold, and steel improperly made in the open hearth. Cracks on the butt of the ingot are rare and usually are due to improper mold design or too high a rate of pouring speed. Cracks at the top of the ingot are caused also by hangers, small fins of metal between the hot top and the ingot mold. Such hangers do not always cause cracks; cases have been noted in which a hanger at least $\frac{1}{2}$ in. thick has failed to produce a crack, although at other times a very thin hanger has caused a crack. The predominating cause of cracks in this kind of ingot is too high a rate of pouring speed from ladle to ingot mold. On the other hand, pouring too slowly can also cause its share of rejections, which usually are referred to as inclusions, or sand. These inclusions come from erosion of the lining of the tapping spout, the interior of the ladle, the nozzle and sleeve brick and from the runner brick through which the metal is bottom-cast. The fact that top-cast ingots show inclusions of sand is evidence that runner brick used in bottom-cast steel are not the only source of contamination. In bottom-cast steel this defect usually shows as inclusions on the skin of the ingot, although occasionally it is found in the interior of the ingot. Brick for use in ladles, tapping spout, runner brick, etc., should show a high fusion point. Such brick is a vital necessity in the steel industry, and it is to be hoped that it may be produced in the near future. When such brick is not obtainable, the steelmaker must adapt his pouring practice to the brick. Steel at high temperatures poured too slowly shows a consistent high percentage of rejections due to sand. Steel at a low temperature, such as at the end of a furnace run, shows a consistent high percentage of rejections due to dirt, unless care is taken to pour very fast. Fig. 4 indicates the relation of cracks and sand with temperature and pouring

speed.   In this case the rejections for sand would have been lower had the pouring speed been increased.

Tests have been made on pouring speed, by carefully comparing results of pouring various groups of ingots, such as eight on a group, six on a group, two on a group and single ingots poured individually.   In all cases, it has been found that as the pouring speed increases, so also does the percentage of rejections due to cracks, while at the same time the percentage of rejections due to sand, etc., decreases.   Each type of steel has its own rate of pouring speed, which depends upon temperature, ingot size and condition of the ingot mold.   Such a rate of speed can be
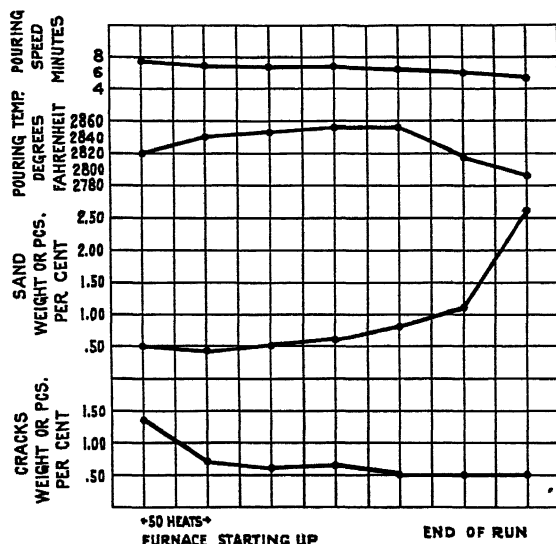
FIG. 4.—CRACKS AND SAND IN RELATION TO TEMPERATURE AND POURING SPEED.

determined by observing a number of heats and comparing the pouring speed with the percentage of rejections.

Fig. 5 shows a typical ingot and runner used for ingots bottom-cast from the steel described in this paper.   A male joint on top of the ingot mold and a female joint on the bottom of the hot top make possible quick and accurate centering of the hot top.   This accurate centering of the hot top is important, first to give an even distribution of metal in the hot top, over the very center of the ingot body, and second, to facilitate the use of an automatic chuck in centering the ingot in the slicing lathe. The interior of the hot top is lined after each heat with a mixture of high-grade silica sand, which is one of the most efficient heat containers. These hot tops are rammed on a jarring machine and the interior is washed with a silica wash, after which they are baked in a drying oven for several hours.   The resulting hot top gives a maximum of insulating value to the metal in the hot top.   Fig. 5 also shows that the stool brick

in the bottom of the ingot mold has the large opening towards the interior of the mold, instead of, as usual, towards the exterior. This opening in the stool brick, shaped with its large opening towards the ingot body, has a tendency to force the particles of sand, slag, etc. suspended in the metal towards the side of the ingot mold, instead of allowing them to lie on the bottom and become entrapped in the freezing metal in the lower section of the mold. The center runner, through which the metal is bottom-cast, is about 2 ft. longer than the total length of the ingot mold and hot top, which enables the steel pourer to maintain a constant rate of pouring speed for the entire ingot, instead of being obliged to slow down on account of the reduction in ferric head in the ladle.
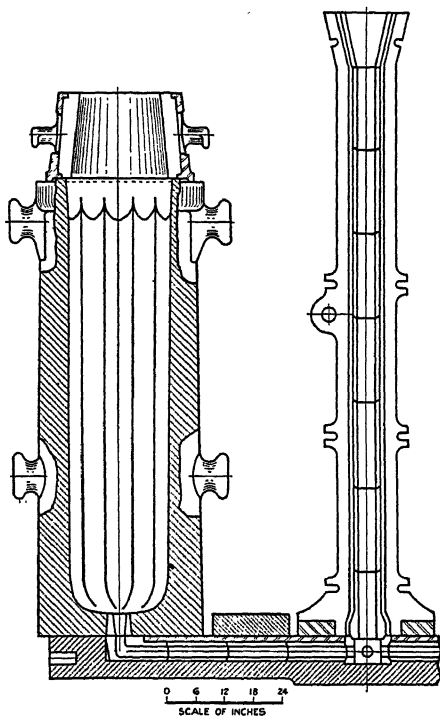
Ingots of the type described, properly cast, and with all precautions taken to ensure a high quality of forging steel, should show a total percentage of rejections due to open-hearth defects of under 2.50 per cent. This figure represents either weight or pieces. Most of these defects are not detected in the open hearth but show up under the forging press, in the rolling mill, or later in the machining operations.

The drop in temperature of steel, after it is tapped into the ladle and before it is poured into ingots, has been a subject of considerable interest. Observations have been made on many heats, and while results are subject to considerable variation, it has been found that steel with a temperature of approximately 2900° F. will lose its temperature at the rate of 6° per min. Steel at a lower temperature, or approximately 2800° to 2850° F., shows a drop of about 3° per min. Some decreases have been noted as high as 10° per min. Possible variations in readings of an optical pyrometer make such temperatures variable, but observations made over a considerable period of time will be valuable to the steel pourer in determining the proper rate of pouring speed for various groups of ingots.

SCALE OF INCHES

FIG. 5.—MOLD AND RUNNER.

On a majority of heats of steel considerable variation in temperature may be found in the same ladle, the steel immediately adjacent to the

slag showing the highest temperature. A typical heat of this type is as follows:

At tapping......... 2.43 p.m., 2920° F.   Group 2 poured.... 2.59 p.m., 2879° F.
Group 1 poured..... 2.52 p.m., 2893° F.   Group 3 poured.... 3.03 p.m., 2849° F.

EFFECT OF ANALYSIS ON REJECTIONS

Final analysis has considerable bearing on the percentage of rejections for cracks, blowy steel and sand. Tests similar to those described here show considerable variation due to silicon content. Observations were made on a large number of heats where pouring practice was held as nearly constant as possible, the only change being variation in silicon content. Table 2 shows some of the most marked variations.

TABLE 2.—*Effect of Silicon on Quality of Steel*

Defects	Percentage of Rejections	
	Average Silicon Content 0.22	Average Silicon Content 0.28
Blowy pieces..............................	0.248	0.051
Cracks...................................	1.072	1.866
Sand.....................................	1.140	1.666
Segregation..............................	0.067	None

A careful analysis of the material on this test shows that some of the material rejected because of cracks was affected by an increase in pouring speed, but the decrease in blowy material, increase in sand and decrease in segregated blocks due to the increase in silicon is noticeable. The increase in sand with the increase in silicon probably is due to the fluxing action of the larger amount of silicon. Doubtless the larger inclusions formed were retained in the steel instead of rising to the surface.

The subject of alloy contamination of basic open-hearth steel is becoming a vital one. Proper selection of raw materials, particularly heavy melting scrap, should give the finished product a total of all alloys—chrome, vanadium, nickel, copper, tin, etc.—of not over 0.10 per cent., which should not prove troublesome.

BASIC OPEN HEARTH VERSUS ACID OPEN HEARTH

Some men believe that the best forging steel can be made only in the acid open-hearth furnace, but during recent years the basic process has been so highly developed that it is possible to produce steel as good as that produced by the acid process; sometimes better. The basic process is strictly a refining process. While selection of raw materials is not as important for the basic open hearth as for the acid open hearth, nevertheless the selection of high-grade materials is reflected in the

finished product. The acid process is a melting process, the finished product, especially the phosphorus and sulfur content, being controlled entirely by the original charge. High phosphorus and sulfur are very undesirable in forging steel. Phosphorus of 0.015 per cent., and often less, and sulfur of 0.02 and less, are common in good basic open-hearth practice. Such low figures are rarely found in acid open-hearth work.

Basic open-hearth forging steel, made with attention to all details, with the proper selection of raw materials, compares in every way with steel made by the acid open-hearth practice. Such basic open-hearth steel, as described in this paper, bottom-cast in molds of the type noted, will show a minimum of segregation, excellent ingot surface, a minimum of pipe and a high yield. The yield should be 90 per cent. or better, and the open-hearth defects should not exceed 2.50 per cent.

DISCUSSION

W. J. REAGAN.—Various questions have been asked regarding particular points in my paper, to which I should like to reply as follows: In ingot-mold work at one time we figured that ⅛ in. was very close tolerance in the making of the ingot mold. Our specifications call for plus or minus ⅟₁₆ in. on inside diameters, and we have no trouble in obtaining it. Inside diameters of ingot molds are very particular in our class of work. The ¼-in. decrease in ingot-mold diameter comes at about 150 heats in the life of a mold. The interior surface seems to decrease rather gradually, up to something like 100 heats, and at that point it remains fairly permanent to 200 heats. It checks very closely with the findings of Mr. Remmers on the permanent growth of cast iron. Referring to the elimination of cracks by the change in mold design, the reason for this has never been found. There has been considerable discussion regarding it. The graphite mixture used as an ingot-mold wash contains about 40 per cent. graphite and a small percentage of fireclay of some sort as a bond.

If you follow the chart (Fig. 3) closely, you will note that some of the points showing exceptionally high iron oxide in the slag indicate clearly a low residual manganese in the bath; high iron oxide in the bath and low residual manganese follow very closely. Some of the points are very noticeable

The statement on page 54, "He *must* tread a straight and narrow path," should be clarified a little. I should say that there is a rather straight and narrow path that he should tread to get the minimum amount of rejections. He does not have to tread the straight and narrow path; in fact, a great many do not. But the path seems to be rather narrow to get the minimum of rejections on high-class forging steel.

We do not have longitudinal cracks. A longitudinal crack is a rarity. I have not seen one for eight or ten years.

Often on the last group (p. 57) we find a higher temperature than the temperature preceding it or possibly two temperatures preceding it, due to the close proximity of the metal to the slag.

R. S. SIMMONS, Monessen, Pa. (written discussion).—We all know the difficulty in making billets of forging quality, and can appreciate the extreme difficulty in making ingots that are to be exposed directly to forging conditions, or surface expansion, without the benefit of any previous hot work. The refinements of open-hearth practice are not nearly so vital and necessary in the manufacture of forging-quality billets as they are in the manufacture of forging-quality ingots. It is possible that the open-hearth charge and working of the heat might be the same in both cases, but the open-

hearth practice thereafter, which is usually applied in the manufacture of forging-quality billets, would, in many cases, be fatal to the manufacture of forging-quality ingots.

For instance, the temperature of the steel at time of tapping is confined to much more narrow limits. Too high a temperature means many cracks, which would render the forging-quality ingots unfit for use, but which would only mean a little more chipping in the manufacture of forging-quality billets. Too low a temperature means countless surface blowholes, which might weld up in the reheating and rerolling for forging-quality billets but which would open up when the ingots were exposed to forging conditions. Then again, flaws can be chipped from steel during some part of the manufacture for forging-quality billets, but chipping flaws from ingots is very dangerous, because minute blowholes are often opened up by chipping and these oxidize deeply when the chipped ingots are reheated.

The speed of pouring is much more important. Ingots that are to be exposed immediately to stresses at right angles to their cross-section must be bottom-cast, in order to obtain the benefit of the slow casting when a number of them are fed through the same center runner. The number of ingots on a group must be carefully decided upon. If more than 20 tons of ingots of normal length, or less than 12 tons of ingots of the same length, are fed through the same center runner the casting in the first case will be too slow and in the second case too rapid. The speed of pouring also must be regulated carefully by the steel pourer, and bad conditions derived from variations in the temperature of the steel can be mitigated to some extent by carefully regulating the amount of steel leaving the ladle.

Brick and sand inclusions in steel are much more disastrous in forging-quality ingots than in forging-quality billets. This nonmetallic matter, if in large enough lumps, will invariably move to the outside, or surface of the ingot, and in the manufacture of forging-quality billets it will obtain the benefit of reduction and elongation before the steel is subjected to the expansion of the surface by forging conditions. Then again, chipping that might prove disastrous to forging-quality ingots could be well applied in some part of the manufacture of forging-quality billets.

The writer heartily agrees with nearly every point Mr. Reagan has made in his paper, and he has merely taken this opportunity to explain why certain variations in open-hearth practice would not be so important in any process other than that which Mr. Reagan describes.

H. STYRI, Philadelphia, Pa.—Mr. Reagan says that there is evident relation between the increase in residual manganese and the increase in slag temperature. I have tried to follow his point but it was a little difficult. If plots have been made in a different manner, for instance, showing statistically that there was some relation, I should like very much to see them.

W. J. REAGAN.—This plot (Fig. 3) contains just a small fraction of the different things that we plotted on this experiment. While possibly it is not clear, if each of the individual heats is followed closely, it will be apparent how the increase in temperature, and especially the increase in iron oxide, affects the residual manganese.

Since plotting this chart, we have separated all this information between two melters who made all of this steel. One of them carries a much higher temperature in his furnace and in his pouring practice than the other, and the higher residual manganese in that case is much more noticeable.

Again, you will notice there is a split in the chart about two-thirds of the way over, and the increased slag temperature is very apparent at that point. The temperature is materially higher, and the residual manganese also is materially higher. The answer to that is the lower amount of manganese added in the final deoxidation. That

is not plotted in this paper. If it were plotted it would show much more clearly the effect of high temperature against the high residual manganese, and, finally, a much smaller quantity of manganese added in the final addition, which is a material saving in open-hearth practice.

E. J. P. FISHER, Peoria, Ill.—Have you experimented at all with a very thin aluminum mold wash?

W. J. REAGAN.—I am sorry to say we have not. We have had some to experiment with, but we have not used it. My belief is that it is considerably harder to handle than the graphite wash. There may possibly be other materials that are easier to handle than graphite, but we have not found them. There has been considerable difficulty in getting the aluminum in solution with a liquid of any kind, to use it in a high-pressure spray gun on molds. Also, many times a preparation of molasses is used as a binder, and when that is applied to the molds at high temperature it blisters; it causes blisters that will eventually be found on the ingots when they are stripped. The graphite with the water as a binder, and the natural binder that it contains, which is a fireclay, does not act in that way. We find no blisters. The pure graphite alone cannot be applied, at least we have found it cannot be, to give a really good surface. I suppose the lack of a binder is the reason.

A. B. KINZEL, New York, N. Y.—What is the cause of the very sudden increase which is best illustrated in the lowest curve of the graph, FeO in metal before spiegel addition, about six heats before the gap?

W. J. REAGAN.—We have tried to solve the question of why we get iron oxide so high on some heats and so extremely low on others, but we have not been able to answer it.

A. B. KINZEL.—It runs along fairly low, with an occasional high point, and all of a sudden it goes up and stays up.

W. J. REAGAN.—One particular point about that heat is that the slag temperature is quite low.

A. B. KINZEL.—I was not referring to one heat, I was referring to the whole series of heats.

W. J. REAGAN.—That is typical of the decreasing temperature in the open hearth. The average temperature on all of the steel is much lower. That is indicated by the decreasing temperature of the slag before the spiegel addition. Naturally the iron oxide in the slag increases.

A. B. KINZEL.—Did you do that intentionally?

W. J. REAGAN.—We just found that out. That bears out a great many of Dr. Herty's theories and is quite remarkable.

L. F. REINARTZ, Middletown, Ohio (written discussion).—Defects in open-hearth ingots have played an important role in the manufacture of steel during the last decade. As the science of steelmaking advances, the necessity for reducing defects and inclusions in steel will be of utmost importance to the industry. Manufacturers of high-grade forging steels have had to contend with this problem to such an extent that many refinements in operations have been worked out by them to meet this demand for clean steel.

Although bottom pouring does not ensure against dirty steel, it does help produce a better surface on the ingot. Furthermore, pouring hazards necessitate the greatest

care in refining and tapping the steel. The method of slicing ingots described by Mr. Reagan is used in other quality plants and provides the best internal inspection possible. By keeping a careful record of each slice, the steelmaker may obtain information needed for improvement in his product.

As usual, the desirability of high-grade raw materials is stressed. Pig iron containing 1 to 1.3 per cent. silicon retards overoxidation during the melting period and provides sufficient temperature at the finish of the heat. Pig iron containing around 2 per cent. manganese improves the quality of the steel. Such pig iron increases the fluidity of the slag and helps remove silicates and nonmetallic impurities. Low sulfur and low phosphorus in the charge means that the operation is not complicated by the melting of excess limestone. In our practice, we are careful to avoid the use of high-magnesia limestone because of the viscous slag it forms.

We believe that forging steel of good quality can be made in a fast furnace. The only provision to be observed is that the operation be properly controlled from an atmospheric and combustion standpoint.

The theory that molds grow smaller in the interior is interesting, but does not check with our experience on larger molds. A year ago the statement was made by several men at the open-hearth meeting of the American Institute of Mining and Metallurgical Engineers that a tar wash in molds caused bad corner cracks in high-carbon ingots. It is instructive to note that this defect was not pronounced in Mr. Reagan's test. It has been our experience that tar coating reduces the effect of splash when pouring top-poured steel ingots. The mold life reported is rather exceptional compared to the common experience of other steelmakers, and leads me to wonder whether these molds were made from direct metal or cast from a cupola. The contention that high manganese in molds increases the life checks practice in French mills.

In some plants, oval ladles have proved desirable because they give a much better lining life than the circular ladles. In either case, thin joints between the bricks are necessary. The use of powdered lime to test out a stopper sounds reasonable and is much to be preferred to the standard practice of using sand, especially when making rimming steel.

We will all agree with Mr. Reagan that good steel must be made in the furnace. Patent deoxidizers and scavengers are no panacea or cure-all for sloppy melting practice. For this reason, killed high-carbon steel must not be worked too hot at the finish of the refining period. The slag must be held as basic as possible but fluid enough to allow gases to escape. Iron oxide in steel is the bane of the melter. Very little is known as yet about the control of this oxide but Dr. Herty and others have shown that iron oxide has a vital influence on the behavior of metal in the furnace and the molds and also later on the physical and chemical properties of the metal.

The author describes clearly the identical difficulties we have had when processing heats that have melted low in carbon and no ore has been required in the bath. We try to repig such heats sufficiently so that some ore may be worked through the bath.

The steelmakers must pay close attention to small details in pit practice to be sure of good results. Unless a melter can be confident of almost perfect pit operations, he cannot give his steel the best attention.

In our practice, tapping 100-ton heats, with sufficient slag covering on top of the metal in the ladle, we have found very little drop in temperature between the metal coming out of the ladle at the start of the pour and at the finish. The large drop in temperature reported by the author is probably due to the small volume of metal in a 40-ton ladle.

The yield of 90 per cent. ingots from charge is better than usually obtained.

The best interests of the industry are served by such frank descriptions as Mr. Reagan has given of basic principles underlying the manufacture of quality steels.

H. D. HIBBARD, Plainfield, N. J. (written discussion).—This is a most interesting paper of a type hoped for, but seldom seen. Dealing with but one kind of steel, its lessons are more applicable in actual work than those which are general for all kinds. It is particularly notable in establishing that basic high-carbon steel may be made at least equal in quality to acid.

The practice of recording results on punched cards is commendable, but, as in all methods of keeping records, the observations recorded, to be valuable and trustworthy, must be made by some competent experienced person who has no control of the operation. It is asking too much of human nature to expect one to frankly admit and record his own mistakes and failures, to accept responsibility for them or to explain them so as to help another to avoid them in the future.

As for high manganese in the crude iron, there may be a practicable upper limit, though some Swedish irons have, or formerly had, 3 or 4 per cent. The question is on the solvent effect of manganese on the gases, and the effect of retained gases on the quality of the steel, subjects on which our ignorance is well-nigh perfect. Residual manganese in the bath metal tends to check the boil, which means that more gases are retained than when the boil is more vigorous.

For silicon in the iron there is also a practicable upper limit, because a too acid slag will retard the elimination of phosphorus from the metal, and will corrode the hearth unduly. With low-silicon mixer metal, the bottom should need but slight repair after a heat; sometimes none.

Statement of the degree of boil at each stage of the typical heat noted would be instructive; say, when first all melted, before and after each ore addition, before the spiegeleisen was added and just before tapping. This, with knowledge of the manganese content in the bath metal at each stage, would be enlightening.

A concrete example or two to illustrate each principle stated would increase the value of the paper to the man in the melting house.

As is common in writings dealing with steelmaking, carbon is said to be "reduced" when it is oxidized.

C. H. HERTY, JR. Pittsburgh, Pa.—I just want to call attention (Mr. Reagan has probably done so) to Fig. 3, which shows how the oxidation of the metal increases for a given carbon as a furnace approaches the end of its campaign. It is rather striking to show how the iron oxide content of the metal increases when the furnace is normally making colder steel than at the first part of the run where the steel is hot.

At the break in the two curves, the iron oxide content of the metal dropped off appreciably. The average was much lower at the start of the new furnace than at the finish of the old furnace. This particular fact is probably the answer to a good many questions which have arisen on the quality of steel made during the last few heats of a furnace campaign, that is, both rimming steel and killed steel, because the same type of iron oxide curve probably holds for low-carbon as well as for high-carbon steel. That brings up a point which may come up later on as to what is the proper time to change a furnace from one grade to another, or, in case you are only making one grade of steel, what is the proper time to take off a furnace, aside from the time element and the cost on the furnace proper, that is to say, the cost on the finished product may be greater than the extra few heats warrant.

W. J. REAGAN.—Answering some of Mr. Reinartz' questions about the ingot molds, whether they are made from cupola or direct metal, probably a small percentage of direct-metal molds are in the average figures we have given, but the majority are cupola metal. There is a material increase in mold life due to direct metal, but we are much more concerned with accuracy of inside diameters than the mold life. I believe that is the only point Mr. Reinartz raised. He did say something about the

decrease in temperature being due to the smaller quantity of metal in a 40-ton ladle. We have felt it was due more to the high temperature we carry, because all our material is bottom-cast. So many steelmakers make top-cast material, and the temperatures are much lower than bottom-cast. The bottom-cast temperatures must be maintained because all of our material must be bottom-cast. If it is not bottom-cast, it is scrapped; it is not used for any purpose. So the melter and the steel pourer play safe to have a much higher temperature than in top-cast production.

Mr. Reinartz mentioned something to the effect that they found they could make just as good steel in a fast-working furnace as in a slower one. I think iron oxide control is the answer to it. We have not found how to control it as yet.

Production of Gray Iron from Steel Scrap in the Electric Furnace

By T. F. BAILY,* CANTON, OHIO

DURING the period of the war, in both this country and Canada, a number of attempts were made to make pig iron from steel scrap in the
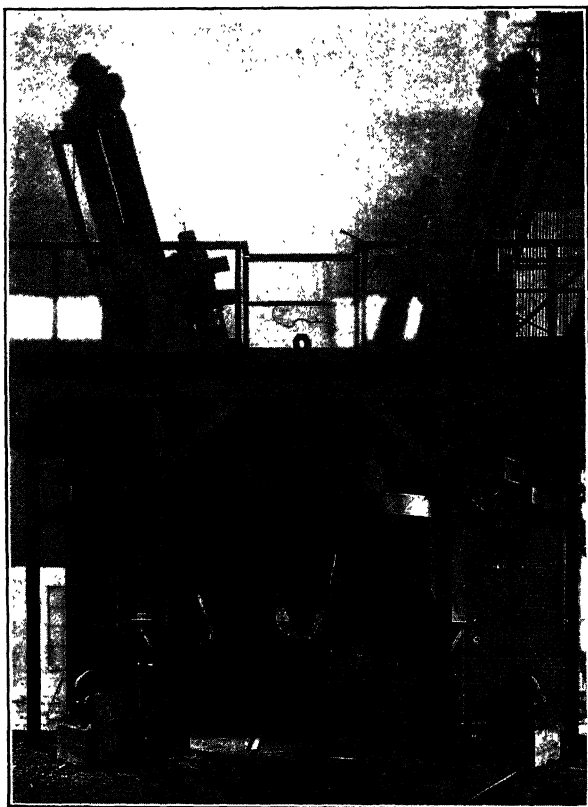

FIG. 1.—EXPERIMENTAL FURNACE. 5000 KW. CAPACITY: 150 TONS 2 PER CENT. SILICON PIG IRON PER DAY.

electric furnace, and a considerable tonnage of white pig iron was produced, the silicon and manganese additions being made with ferroalloys; but it is believed that the experiments conducted at Canton, Ohio, in

* Baily Furnace Co.

1927 were the first successful attempts at producing gray iron with silicon and manganese additions made from the oxides of these metals reduced directly in the furnace, although a number of years ago a smaller experimental unit was operated by the same method and produced gray cast iron of low silicon and manganese content.

The furnace used for this experimental operation was of the shaft type (Fig. 1). It had three electrodes in the top of the furnace set at an
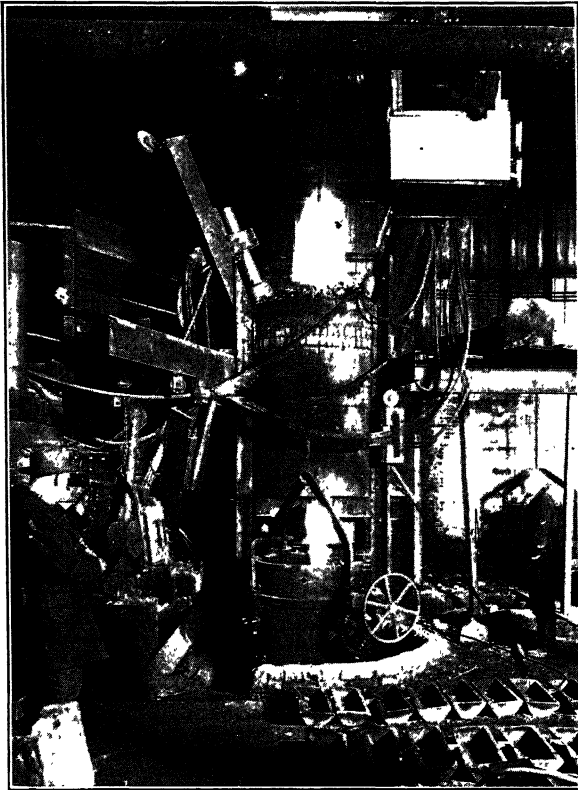
FIG. 2.—EXPERIMENTAL FURNACE. 800 KW. CAPACITY: 1 TON PER HOUR OF 2 PER CENT. SILICON PIG IRON FROM ALL STEEL SCRAP CHARGE.

angle of about 15° and one electrode in the bottom. The furnace shaft was filled with coke so that the arcs of the three upper electrodes played directly on the top of the coke column, the current flowing from electrode to electrode at the top, and as the furnace was star connected a certain portion of the current went to the bottom electrode. The height of the coke column was approximately 6 ft.; the diameter of the furnace at the top inside was 4 ft. and at the bottom, 2 ft. Material was charged through a hole in the center of the roof and lay on the top of the coke column, where it was melted by the three upper arcs and immediately

passed down in small streams or globules through the heated coke or carbon, rapidly absorbing carbon from the coke column to the saturation point, reducing the oxides of manganese, silicon and phosphorus in the charge and passing through the calcium slag for the reduction of the sulfur content. In all, over 100 heats were made, all of which showed substantially full carbon saturation, all producing gray iron with silicon content of from 1 to 3 per cent.

Test bars were cast from a number of these heats and test bars were also cast from the pig iron rerun in a cupola at some of the local foundries. The results of these tests are given in the accompanying tables and photomicrographs.
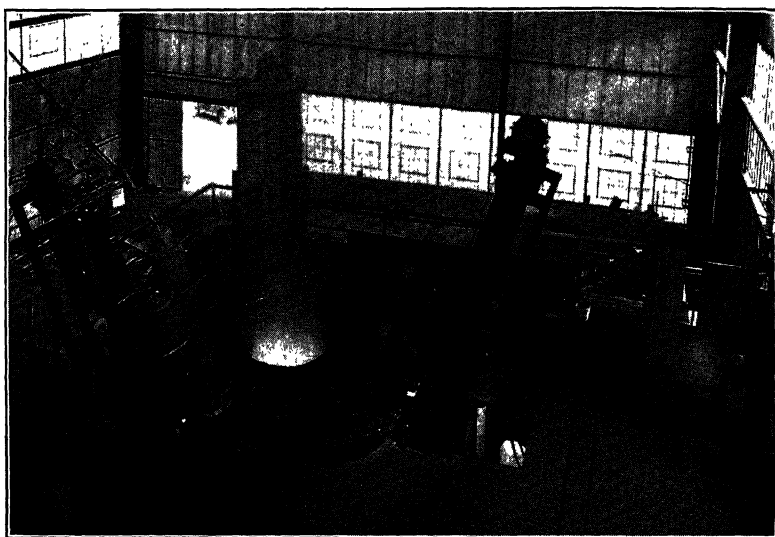
FIG. 3.—TOP OF 5000-KW. UNIT.

In Table 1, covering heats 1, 7, 21, 28 and 37, the reduction of the oxides to metal is clearly shown. For instance, beginning with heat 1, where the only change in the analysis of the material charged was an increase in carbon and silicon and a change in the sulfur content due to the sulfur in the initial coke charge, the silicon increase caused by the sand charged brought this element from 0.08 to 1.98, the carbon was raised from 0.19 to 3.26 and the sulfur increased from 0.036 to 0.164.

Heat 7 had an increase in the amount of sand charged and an addition of 80 lb. of lime, the silicon was increased to 2.95 and the sulfur reduced to 0.032. It is interesting to note that even though the slag was very acid, the sulfur was low. The silica content of the slag was above 50 per cent., the alumina 12.76 per cent. and the calcium oxide, 36 per cent.

TABLE 1.—*Effect of Oxides for Alloy Additions and for Sulfur Removal*

	Heat 1, Pounds	Heat 7, Pounds	Heat 21, Pounds	Heat 28, Pounds	Heat 37, Pounds
CHARGE					
Steel scrap......................	800	2000	2300	2300	2300
Coke............................		114	250	350	285
Lime...........................		80	100	100	
Sand...........................	87	190	150	150	100
Ferromanganese.................		10	9	9	
Phosphate rock.................			75	100	100
Basic open-hearth slag..........					200
Fluorspar......................		5			
ANALYSIS OF STEEL SCRAP CHARGED					
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Carbon.........................	0.19	0.19	0.26	0.36	0.30
Manganese......................	0.45	0.45	0.44	0.56	0.64
Sulfur.........................	0.036	0.036	0.041	0.045	0.042
Phosphorus.....................	0.097	0.097	0.033	0.014	0.025
Silicon........................	0.08	0.08	0.07	0.18	0.13
Oxygen.........................	0.47	0.47	0.50		
Chromium......................			0.04	0.54	0.284
Nickel.........................			0.08	1.28	0.64
Iron...........................	98.60	98.60	98.50	97.00	97.25
Oil and moisture...............	3.00	3.00	2.8	1.10	0.50
ANALYSIS OF PIG IRON PRODUCED					
Carbon.........................	3.26	3.88	4.00	3.77	4.01
Manganese......................	0.32	0.82	0.79	0.76	0.72
Sulfur	0.164	0.032	0.036	0.037	0.026
Phosphorus.....................	0.098	0.107	0.396	0.450	0.636
Silicon........................	1.98	2.95	2.28	2.09	1.88
Chromium......................			0.06	0.42	0.36
Nickel.........................			0.11	0.99	1.07
ANALYSIS OF SLAG					
SiO_2...........................		50.32	39.76	38.64	37.82
Al_2O_3..........................		12.76	1.19	18.04	20.48
Fe.............................					1.34
CaO...........................		35.92	39.02	41.32	37.78
MgO...........................		Bases	Bases	Bases	Bases
S.............................				0.85	

On heat 21, the lime was increased to 100 lb. and the sand was decreased to 150 lb.; the silicon was 2.28, the sulfur 0.036, and the slag substantially 40 per cent. silica, 1 per cent. alumina, and 39 per cent. calc'um oxide. The phosphorus was built up from 0.033 to 0.396 by the addition of phosphate rock to the charge.

On heat 28, the scrap was changed to a chrome-nickel scrap having 0.54 chromium and 1.28 nickel; the lime and sand charged were the same, and the phosphate rock charged was increased to 100 lb. The addition of the extra 25 lb. of phosphate rock over heat 21 increased the phosphorus content in the metal from 0.396 to 0.450.

On heat 37, the sand was reduced to 100 lb. and basic open-hearth slag was used for the calcium content in place of lime, the phosphate rock remaining the same as in the previous heat. The phosphorus content was raised by the phosphorus in the open-hearth slag from 0.450 in heat 28 to 0.636 in heat 37; the sulfur which was 0.037 in heat 28, where lime was used, was reduced to 0.026 in heat 37, where open-hearth slag was used. The slag was substantially 38 per cent. silica, 20 per cent. alumina and 38 per cent. calcium oxide. Also, no ferromanganese was charged in heat 37 while 9 lb. had to be added to the charge in heat 28 to increase the manganese content; in heat 28 this was 0.76, while in heat 37 sufficient manganese was recovered from the open-hearth slag to take the place of the 9 lb. of ferromanganese used in heat 28.

Repeated duplication of these charges indicates clearly that the phosphorus and manganese can be recovered readily from basic open-hearth slag in this type of furnace, that the lime of the slag can be used effectively for sulfur removal, that the silicon can be increased to any amount by the addition of sand, and the carbon content of the heat brought up to full saturation for any given silicon content; it being understood, of course, that sufficient carbon is charged to take care of the carbon requirement both for the reduction of the oxides and for saturating the bath itself.

Table 2 shows the analyses of 20 consecutive heats in which the carbon, silicon, phosphorus and manganese additions were made as outlined, and the sulfur content was kept below 0.044. The materials charged, the power consumption and the metal produced on these heats are listed in Table 3. The average power consumption for these 20 heats was 1005 kw-hr. per gross ton of pig iron produced of an average analysis of 3.89 C; 2.46 Si; 0.032 S; 0.465 P; 0.775 Mn; 0.04 Cr; 0.06 Ni. The average yield of pig iron was about 93 per cent. of the scrap charged, and the electrode consumption was 9 lb. of graphite electrodes per gross ton of pig iron produced.

On a furnace of commercial capacity, this power consumption would readily come under 750 kw-hr. per gross ton of pig iron produced and the metal yield would be considerably higher, because with the experi-

mental furnace an appreciable amount of metal was lost, on account of the small casts.

While all these heats were run with steel scrap or borings, it is believed that this same type of furnace would work equally well on sponge iron, and that the power consumption of 750 kw-hr. per gross ton would be a fair figure for the production of pig iron of the silicon, manganese, phosphorus and carbon content given in the tables, based on the silicon addition being made from sand, the manganese from manganese ore or basic open-hearth slag, and the phosphorus from phosphate rock.

TABLE 2.—*Analysis of Electric-furnace Pig Iron Made from Steel Scrap*

Cast No.	C, Per Cent.	Si, Per Cent.	S, Per Cent.	P, Per Cent.	Mn, Per Cent.	Cr, Per Cent.	Ni, Per Cent.	Slag				
								SiO_2 Per Cent.	Al_2O_3 Per Cent.	Fe Per Cent.	CaO Per Cent.	MgO Per Cent.
100	3.96	1.94	0.030	0.577	0.67	0.04	0.05	42.16	13.46	0.67	41.42	Bases
101	4.02	2.38	0.023	0.464	0.91	0.05	0.07	37.78	11.88	0.67	47.38	Bases
102	4.01	2.18	0.036	0.403	0.63	0.05	0.06	40.72	11.87	0.34	44.92	Bases
103	4.06	3.39	0.024	0.477	0.79	0.04	0.06	40.08	10.39	0.34	39.68	7.36
104	3.96	2.64	0.027	0.597	0.83	0.05	0.07	42.78	11.37	0.33	43.34	Bases
105	4.38	2.23	0.022	0.470	0.85	0.04	0.06	40.16	11.17	0.33	46.20	Bases
106	3.80	2.22	0.026	0.540	0.75	0.05	0.05	39.98	10.97	0.30	46.58	Bases
107	4.13	2.26	0.025	0.614	0.82			40.64	11.79	0.33	45.10	Bases
108	3.93	1.97	0.031	0.438	0.78			41.42	13.57	0.33	42.54	Bases
109	3.79	2.14	0.036	0.523	0.85			40.38	11.02	0.56	45.80	Bases
110	4.03	1.92	0.031	0.620	0.80	0.08	0.12			0.67		
111	3.87	2.27	0.035	0.456	0.79	0.09	0.16	39.16	16.73	0.44	41.48	Bases
112	3.86	2.09	0.040	0.412	0.83	0.09	0.10			0.33		
113	3.94	2.09	0.039	0.426	0.72	0.08	0.17			0.27		
114	3.59	3.38	0.044	0.333	0.69	0.06	0.12	46.28	16.41	0.63	35.41	Bases
115	3.96	3.33	0.031	0.368	0.76					0.37		
116	3.65	2.95	0.027	0.481	0.77			40.28	14.30	0.42	42.88	Bases
117	3.78	2.75	0.036	0.388	0.77	0.09	0.13			0.33		
118	3.51	2.53	0.033	0.357	0.75			40.28	14.30	0.37	42.88	Bases
119	3.62	2.57	0.036	0.359	0.75							

All the raw material used was of the cheaper variety, such as sheet clippings, long turnings, No. 1 and No. 2 busheling, and cast iron borings; no heavy iron scrap or steel scrap was used because this material demanded a higher price in the market than the lighter grades mentioned and did not seem to be so well adapted commercially for the production of pig iron.

One noticeable feature was that substantially all the chromium and nickel found in the scrap was recovered, as shown in Table 4, due undoubtedly to the fact that the material from the time it entered the furnace was in a completely reducing atmosphere until cast. The average sulfur analysis of the heats run without lime was above 0.10 and the phosphorus was about 0.10; the latter element was built up by the

TABLE 3.—*Charge, Power Consumption and Yield of Metal on Heats Listed in Table 2*

Heat No.	Charge						Power Consumption, Kw-hr.	Metal Produced, Pounds
	Scrap, Pounds	Coke, Pounds	Fluorspar, Pounds	Basic Slag, Pounds	Sand, Pounds	Phosphate Rock, Pounds		
100	2300	200		200	150	80	915	2122
101	2300	None		200	150	80	940	2118
102	2300	300	2½	200	150	80	1090	2255
103	2300	170	2½	200	150	80	1000	2175
104	2300	170	2½	200	100	80	940	2350
105	2300	250	2½	200	100	80	910	2329
106	2300	225	2½	200	100	80	845	2163
107	2300	225	2½	200	100	80	865	2117
108	2300	150	2½	200	100	80	790	2148
109	2300	150	2½	200	100	80	1010	2252
110	2300	225	2½	200	100	80	805	1675
111	2300	150	2½	200	100	80	1195	2310
112	2300	175	2½	200	100	45	1010	2361
113	2300	175	2½	200	100	45	760	1590
114	2300	300	2½	200	100	45	1430	2284
115	2300	150	2½	200	100	45	830	1862
116	2300	150	2½	200	100	45	800	2339
117	2300	150	2½	200	100	45	940	1939
118	2300	225	2½	200	100	45	1010	1868
119	2300	200	2½	200	100	45	1100	2469

TABLE 4.—*Electric Heat 31*

Casting Temperature: Metal, 2650° F.; slag, 2710° F.

Charge

	C Graphitic, Per Cent.	C Combined, Per Cent.	C Total, Per Cent.	Mn, Per Cent.	S, Per Cent.	P, Per Cent.	Si, Per Cent.	Cr, Per Cent.	Ni, Per Cent.	O, Per Cent.	Fe, Per Cent.	SiO₂, Per Cent.	Al₂O₃, Per Cent.	CaO Per Cent.	MgO, Per Cent.
2300 lb. steel scrap		0.36		0.56	0.045	0.014	0.18	0.54	1.28		97.00				
150 lb. coke.......		86.95			0.99	0.019					0.80	6.16	3.20	0.25	0.17
100 lb. lime												0.81	0.74	81.60	12.20
150 lb. sand.......												94.32	3.96	0.80	0.71
9 lb. ferromanganese.....				80.00											
100 lb. phosphate rock.......						14.88				19.20	13.20	5.32	3.94	37.24	0.80

Product

	Metal											Slag			
Pig iron...........	3.37	0.38	3.75	0.78	0.045	0.545	2.12	0.37	1.23						
Slag..............											0.33	39.92	21.77	34.84	

TABLE 5.—*Electric Heat* 100
Casting Temperature: Metal, 2550° F.; slag, 2600° F.

Charge

	C graphitic, Per Cent.	C combined, Per Cent.	C Total, Per Cent.	Mn, Per Cent.	S, Per Cent.	P, Per Cent.	Si, Per Cent.	Cr, Per Cent.	Ni, Per Cent.	O, Per Cent.	Fe, Per Cent.	SiO₂, Per Cent	Al₂O₃, Per Cent.	CaO, Per Cent.	MgO, Per Cent
2300 lb. steel scrap		0.80		0.61	0.042	0.072	0.07	0.09	0.10	3.86	94.00				
200 lb. coke....		86.95			0.99	0.019					0.80	6.16	3.20	0.25	0.17
200 lb. basic open-hearth slag				3.72		0.488					28.50	10.16	3.33	33.84	8.56
150 lb. sand.......												94.32	3.96	0.80	0.71
80 lb. phosphate rock.......						14.88				19.20	13.20	5.32	3.94	37.24	0.80

Product

	Metal											Slag			
Pig iron..........	3.38	0.34	3.72	0.653	0.047	0.472	1.91	0.064	0.054	0.007	93.12				
Slag..............											0.67	42.16	13.46	41	42

TABLE 6.—*Electric Heat* 116
Casting Temperature: Metal, 2560° F.; slag, 2610° F.

Charge

	C Graphitic, Per Cent.	C combined, Per Cent.	C Total, Per Cent.	Mn, Per Cent.	S, Per Cent.	P, Per Cent.	Si, Per Cent.	Cr, Per Cent.	Ni, Per Cent.	O, Per Cent.	Fe, Per Cent.	SiO₂, Per Cent.	Al₂O₃, Per Cent.	CaO, Per Cent.	MgO, Per Cent.
2300 lb. steel scrap			2.60	0.65	0.059	0.128	1.26	0.07	0.07	4.02	91.10				
150 lb. coke.......		86.95			0.99	0.019					0.80	6.16	3.20	0.25	0.17
200 lb. basic open-hearth slag				3.72		0.488					28.50	10.16	3.33	33.84	8.56
100 lb. sand.......												94.32	3.96	0.80	0.71
45 lb. phosphate rock.......						14.88				19.20	13.20	5.32	3.94	37.24	0.80
2½ lb. fluorspar...															

Product

	Metal											Slag			
Pig iron..........	3.27	0.28	3.55	0.745	0.052	0.540	2.83	0.084	0.070	0.006	92.123				
Slag..............											0.42	40.28	14.30	42.88	
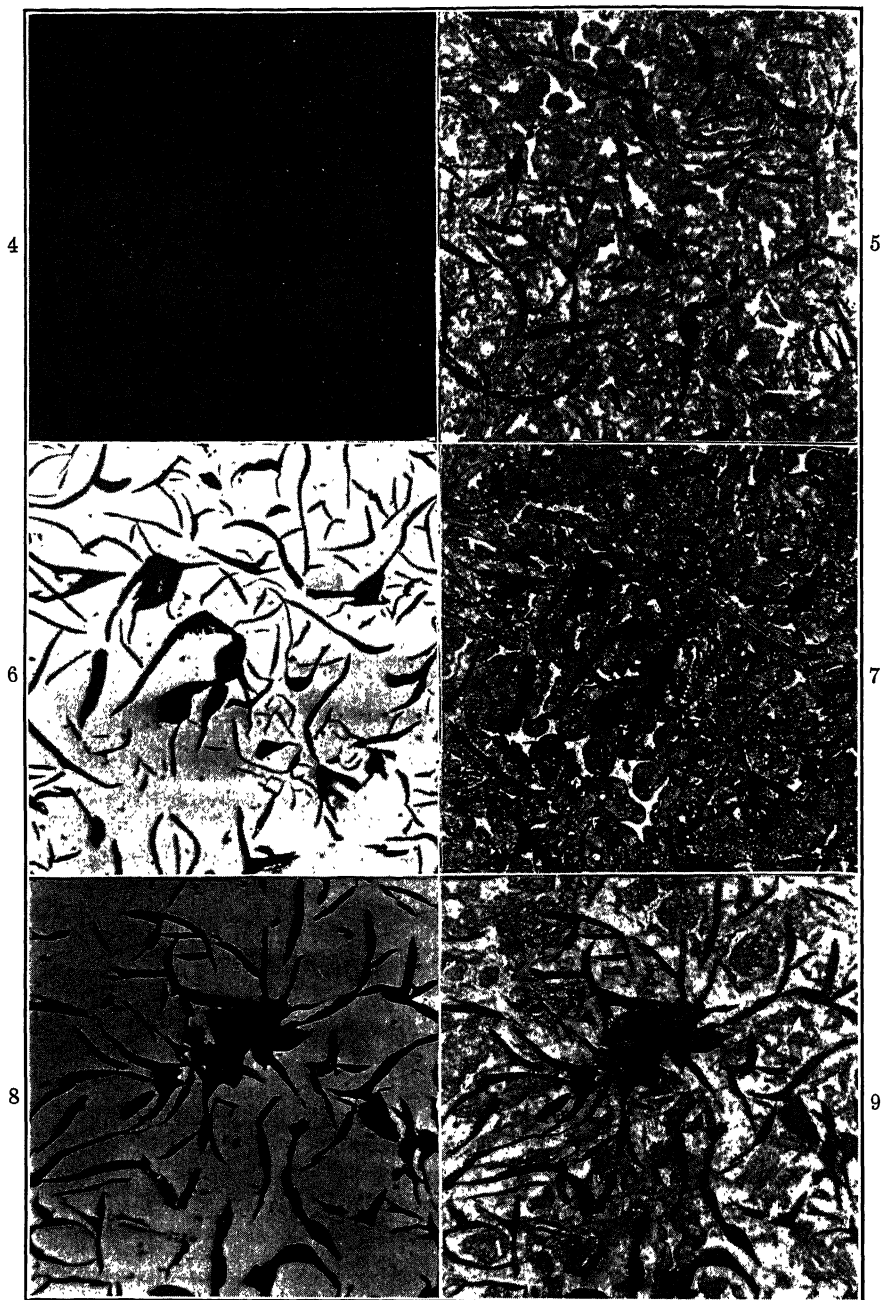
FIGS. 4–7.—TEST BARS CAST DIRECTLY FROM ELECTRIC FURNACES.
Figs. 4 and 6 unetched; Figs. 5 and 7 etched.
FIGS. 8–9.—TEST BARS MADE IN CUPOLA FROM BLAST-FURNACE IRON.   80 PER CENT.
PIG; 20 PER CENT. GATES AND RISERS.
Fig. 8 unetched; Fig. 9 etched.   Made at Wright Chain Co., Lisbon, Ohio.

addition of phosphate rock and sufficient lime slag was added to hold the sulfur under 0.04, although there was no difficulty in getting sulfur as

TABLE 7.—*Blast-furnace Heat* 2.60
Iron Run in Cupola at Wright Chain Co.
Charge: 80 per cent. Cherry Valley special pig iron; 20 per cent. gates and risers

C Graphitic, Per Cent.	C Combined, Per Cent.	C Total, Per Cent.	Mn, Per Cent.	S, Per Cent.	P, Per Cent.	Si, Per Cent.	Cr, Per Cent.	Ni, Per Cent.	N, Per Cent.	Fe. Per Cent.
3.33	0.015	3.345	0.686	0.070	0.794	2.44	0.052	0.045	0.006	92.562

TABLE 8.—*Electric Heat* 2.68
Iron Run in Cupola at Wright Chain Co.
Charge: 80 per cent. electric pig iron made from steel scrap; 20 per cent. gates and risers

C Graphitic, Per Cent.	C Combined, Per Cent.	C Total, Per Cent.	Mn, Per Cent.	S, Per Cent.	P, Per Cent.	Si, Per Cent.	Cr, Per Cent.	Ni, Per Cent.	N, Per Cent.	Fe, Per Cent.
3.22	0.28	3.50	0.549	0.055	0.480	2.79	0.085	0.105	0.004	92.433

TABLE 9.—*Special Blast-furnace Heat* 1
Iron Run in Cupola at Deming Foundry Co.
Charge

	C Graphitic, Per Cent.	C Combined, Per Cent.	C. Total, Per Cent.	Si, Per Cent.	Mn, Per Cent.	S, Per Cent.	P, Per Cent.	Cr, Per Cent.	Ni, Per Cent.
700 lb. Clair.......				2.53	0.95	0.027	0.230		
600 lb. Cherry Valley.........				2.75	0.60	0.025	0.600		
700 lb. Clair.......				2.20	0.70	0.032	0.217		
100 lb. Steel scrap..				2.25					
900 lb. Iron scrap..					0.62	0.065	0.409		
3000 lb.............				2.35	0.72	0.039	0.348		

Product

	C Graphitic, Per Cent.	C Combined, Per Cent.	C. Total, Per Cent.	Si, Per Cent.	Mn, Per Cent.	S, Per Cent.	P, Per Cent.	Cr, Per Cent.	Ni, Per Cent.
	3.25	0.34	3.59	2.17	0.626	0.076	0.396	0.015	Trace

low as 0.025, and with a richer lime slag, a sulfur content as low as 0.014 was obtained.

Tables 5 and 6 show the results from test bars from two heats cast directly from the furnace; Table 7, a heat of high-grade blast-furnace iron run through the cupola, and Table 8, a heat of electric pig iron rerun in the cupola; these last two heats consisting of 80 per cent. pig iron and 20 per cent. sprues and gates.
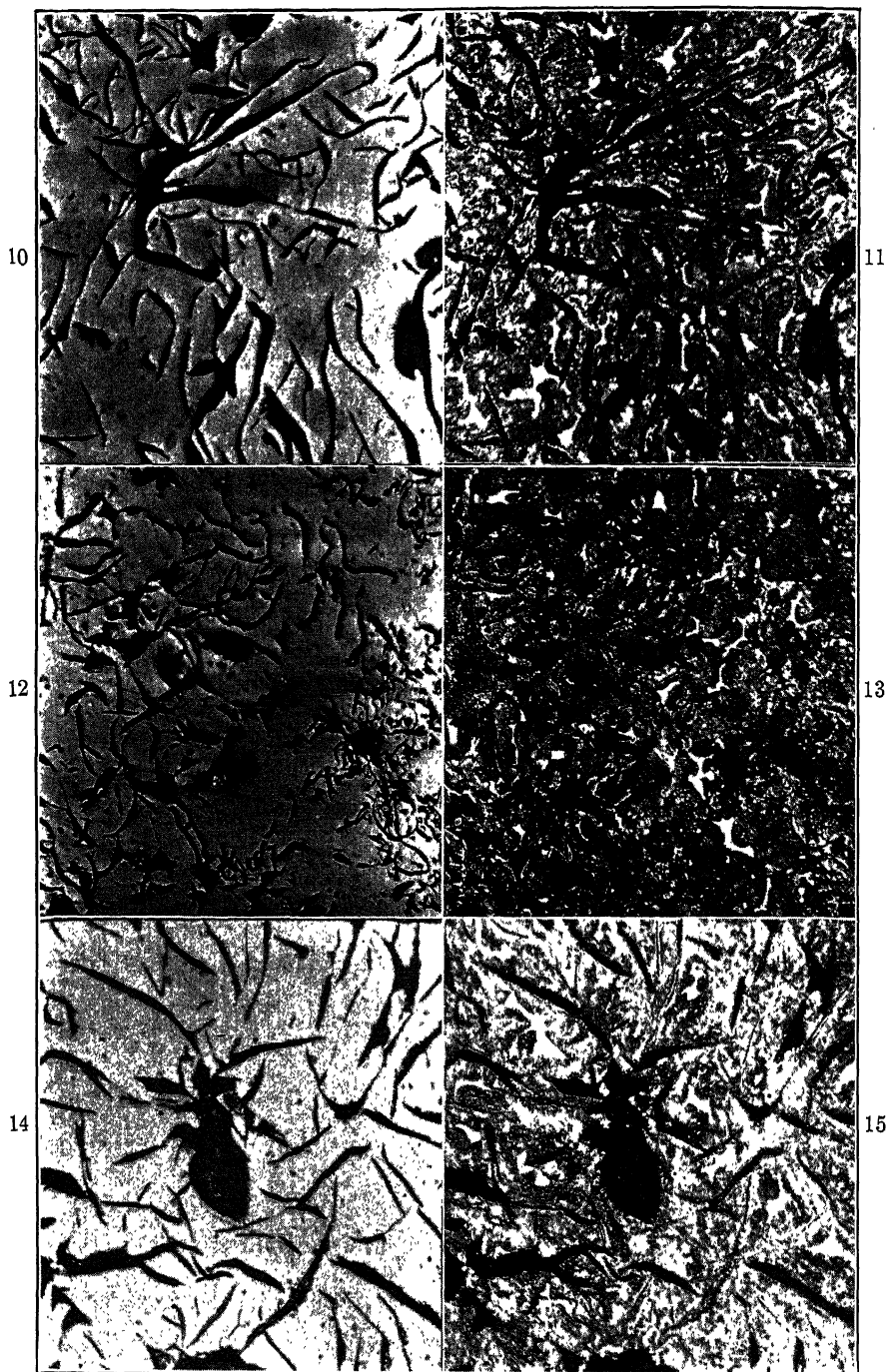
FIGS. 10–15.—CAPTIONS ON OPPOSITE PAGE.

Tables 9 and 10 show the results of some test bars cast in another foundry. The results of tests on electric iron are given in Table 10 and the results of tests on blast-furnace iron in Table 9. It will be noted

TABLE 10.—*Special Electric Heat* 3

Iron Run in Cupola at Deming Foundry Co.

Charge

	C Graphitic, Per Cent.	C Combined, Per Cent.	C Total, Per Cent.	S, Per Cent.	Mn, Per Cent.	S, Per Cent.	P, Per Cent.	Cr, Per Cent.	Ni, Per Cent.
2100 lb. electric pig..				2.43	0.82	0.032	0.450		
900 lb. sprues and gates.......				2.20	0.56	0.068	0.480		
3000 lb.............				2.36	0.77	0.042	0.460		

Product

C Graphitic, Per Cent.	C Combined, Per Cent.	C Total, Per Cent.	S, Per Cent.	Mn, Per Cent.	S, Per Cent.	P, Per Cent.	Cr, Per Cent.	Ni, Per Cent.
3.25	0.44	3.69	2.18	0.594	0.071	0.432	0.025	0.001

TABLE 11.—*Comparison of Chemical Analyses and Physical Properties of Electric Pig Iron and Blast-furnace Iron*

	Heat	Si, Per Cent.	P, Per Cent.	S, Per Cent.	Mn, Per Cent.	C Combined, Per Cent.	C Graphitic, Per Cent.	Ni, Per Cent.	Cr, Per Cent.	Brinell Hardness	Load, Lb. per Sq. In.	Deflection, Inches	Sp. Gr.	Ultimate Strength
Electric pig iron cast directly from furnace.............	100	1.91	0.472	0.047	0.653	0.34	3.38	0.054	0.064	144	2,650	0.151	7.085	23,460
Electric pig iron cast directly from furnace.............	116	2.83	0.540	0.052	0.745	0.28	3.27	0.070	0.084	179	2,680	0.164	7.080	15,060a
Blast-furnace iron rerun in cupola.......	2.60 2.60	2.44	0.794	0.070	0.686	0.15	3.33	0.045	0.052	163 143	3,285 2,840	0.180 0.182	7.024	20,530 18,850
Electric pig iron rerun in cupola.........	2.68 2.68	2.27	0.500	0.060	0.556	0.30	3.30	0.058	0.069	149 159	3,340 2,600	0.192 0.156	7.105	21,390 25,130
Blast-furnace iron rerun in cupola.......	1 1	2.17	0.396	0.076	0.626	0.34	3.25	Tr.	0.015	163 163	3,200 3,650	0.158 0.122		20,060 21,870
Electric pig iron rerun in cupola.........	3 3	2.18	0.432	0.071	0.594	0.44	3.25	0.001	0.025	159 156	3,900 3,150	0.182 0.155		20,040 18,280

a Full of blowholes.

that heat 1 made from high-grade blast-furnace iron had a deflection of 0.158, while heat 3 made from electric iron had a deflection of 0.182,

FIGS. 10–11.—TEST BARS MADE IN CUPOLA FROM ELECTRIC-FURNACE IRON RERUN IN CUPOLA. 80 PER CENT. ELECTRIC PIG; 20 PER CENT. GATES AND RISERS. Fig. 10 unetched; Fig. 11 etched. Made at Wright Chain Co., Lisbon, Ohio.

FIGS. 12–13.—BLAST-FURNACE PIG IRON RERUN IN CUPOLA. TWO-THIRDS FURNACE PIG IRON; ONE-THIRD IRON AND STEEL SCRAP. Fig. 12 unetched; Fig. 13 etched. Made by Deming Co.

FIGS. 14–15.—ELECTRIC-FURNACE IRON RERUN IN CUPOLA. TWO-THIRDS ELECTRIC PIG IRON; ONE-THIRD IRON AND STEEL SCRAP. Fig. 14 unetched; Fig. 15 etched. Made by Deming Co.

the Brinell hardness of the blast-furnace iron being 163, and that of the electric iron, 159.

Table 11 gives comparative figures on the Brinell hardness, deflection and ultimate strength of electric iron cast directly from the furnace, electric iron rerun in the cupola, and blast-furnace iron rerun in the

TABLE 12.—*Proximate and Structural Compositions of Heats Shown in Tables 5 to 10*

	Heat 100, Per Cent.	Heat 116, Per Cent.	Heat 2.60 Per Cent.	Heat 2.68, Per Cent.	Heat 1, Per Cent.	Heat 3, Per Cent.
Proximate Composition						
Silicide of iron........	5.73	8.49	7.32	6.81	6.51	6.54
Phosphide of iron.....	3.03	3.47	5.10	3.21	2.542	2.773
Manganese sulfide....	0.13	0.14	0.19	0.16	0.207	0.193
Manganese carbide....	0.61	0.70	0.61	0.49	0.530	0.505
Chromium carbide....	0.07	0.09	0.06	0.07	0.016	0.027
Iron carbide..........	4.35	3.45	1.50	3.90	4.560	6.075
Graphite.............	3.38	3.27	3.33	3.30	3.25	3.25
Nickel..............	0.054	0.07	0.04	0.058	Trace	0.001
Nitrogen.............	0.007	0.006	0.006	0.006		
Iron................	82.649	80.314	81.844	81.996	82.385	80.64
	100.000	100.000	100.000	100.000	100.000	100.000
Structural Composition by Weight						
Pearlite..............	39.23	33.07	16.93	34.79	39.38	51.53
Ferrite...............	52.54	58.12	71.61	56.75	52.75	40.71
Graphite.............	3.38	3.27	3.33	3.30	3.25	3.25
Steadite..............	4.72	5.40	7.94	5.00	3.96	4.32
Manganese sulfide.....	0.13	0.14	0.19	0.16	0.21	0.19
	100.00	100.00	100.00	100.00	100.00	100.00
Structural Composition by Volume						
Pearlite..............	36.09	30.42	15.58	32.01	36.64	47.41
Ferrite...............	46.77	51.92	63.30	50.70	47.43	36.25
Graphite.............	10.98	10.63	10.82	10.72	10.56	10.56
Steadite..............	5.90	6.75	9.92	6.25	4.95	5.40
Manganese sulfide.....	0.26	0.28	0.38	0.32	0.42	0.38
	100.00	100.00	100.00	100.00	100.00	100.00

same cupola. Table 12 gives the structural composition of the various heats. It will be noted that all the electric-furnace iron, whether cast directly from the furnace or rerun in the cupola, had a high pearlitic constituent, always running above 30 per cent., at least 10 per cent. higher than the blast-furnace iron rerun in the cupola. Brinell hardness in all cases was slightly under that of blast-furnace iron of the same chemical composition and the machining qualities of the electric iron were equal to those of the blast-furnace iron, if not actually superior.

The electric iron cast directly from the furnace or rerun in the cupola had a higher deflection than blast-furnace iron of the same chemical composition, even though the conditions surrounding the casting of the test bars from the electric furnace were by no means ideal, as these bars were all cast in very cold weather and sometimes in frozen molds.

One of the outstanding characteristics of this iron cast in chilled molds was that, regardless of the temperature of the mold, there was little if any evidence of chill in the iron.

TABLE 13.—*Comparison of Transverse and Deflection Tests of Electric Heat* 116 *and a Cupola Heat in a Typical Motor-car Foundry*

ELECTRIC HEAT 116		TYPICAL CUPOLA HEAT	
Charge			
	Per Cent.		Per Cent.
Steel turnings................	50	6 per cent. silicon pig............	7.50
Cast iron borings.............	50	Toledo malleable pig............	36.00
		Iron scrap.....................	30.00
		Borings.......................	20.00
		Steel scrap....................	6.50
Analysis of Metal			
	Per Cent.		Per Cent.
Carbon........................	3.55	....	3.40
Manganese....................	0.745	....	0.74
Sulfur........................	0.052	....	0.033
Phosphorus...................	0.540	....	0.43
Silicon.......................	2.83	....	2.64
Chromium....................	0.084		
Nickel........................	0.070		
Physical Properties			
Transverse...................	2680 lb.	...............2800 lb.	
Deflection...................	0.164 in.	...............0.120 in.	

The specific gravity of the electric iron seemed to be slightly higher than of blast-furnace iron. This again may be noted in Table 11, where the blast-furnace iron denoted by mark "2.60" had a specific gravity of 7.024 as compared with the lowest value in any of the electric iron of 7.08 for the test bars made directly from the furnace, and above 7.105 for the electric iron rerun in the same cupola and under the same conditions as iron indicated by mark "2.60."

Table 13 gives a comparison of electric iron cast directly from the furnace and a typical cupola heat of a foundry making gray iron castings for motor-car parts. The deflection on the electric iron, even though

slightly higher in silicon than the cupola metal, was 0.164 compared with a cupola melt of 0.120.

It is believed that in localities where there is a demand for pig iron and where scrap steels can be obtained at a relatively low price, electric pig iron could be produced economically, of a quality not possible to produce by the blast furnace, and that the electric iron can be cast directly from the furnace, with physical properties superior to those of iron produced in the cupola.

DISCUSSION

J. T. MacKenzie, Birmingham, Ala.—From a direct casting standpoint, these carbons are too high. I see in the first heat the carbon tapped out at 3.26. Does Mr. Baily know why that is, and if so, can he do it every time?

Another possibility in the utilization of steel scrap for a foundry is in cupola melting with subsequent refinement in the electric furnace. You know that with petroleum cokes steel scrap can be melted out easily with 4 per cent. carbon from the cupola. Of course, with 2 or 3 per cent. sulfur in the cokes, there is a terribly high sulfur content and good temperatures cannot be obtained with them, but the combination would seem to be attractive under such conditions.

I have obtained 4.38 per cent. carbon on 100 per cent. steel scrap through a cupola with petroleum coke which ran something over 12 per cent. volatile but still was strong enough to support a light burden.

Member.—I had the same question to ask; that is, whether or not it is possible to produce a lower carbon, or control it. In addition, I was wondering if it is possible in the furnace to provide for superheating in order to break down the graphite nuclei.

T. F. Baily.—Heat No. 1, which was lower in carbon, was rather cold, and I found in earlier experiments that the temperature and time are the vital factors in the amount of carbon, because in some early experiments on the smaller furnace we reached nearly 8 per cent. carbon in the pig iron, by running the carbon resistor up to about 4200° C. and tapping at that temperature. The pyrometer readings were made with a Leeds & Northrup optical pyrometer, so they were fairly accurate.

As to maintaining low carbons with sufficient temperature and rapid operation, that can be done by using a hard carbon instead of porous coke, so as to present less total surface to the melting that is going through. For instance, in this particular furnace there is probably less than one minute from the time the scrap is melted until it is down at the bottom of the furnace. It trickles through and comes in contact with a very big surface of incandescent carbon, compared with the volume of metal running at one time, and that probably accounts for the rapid absorption of the carbon.

Referring to the melting of steel scrap in a cupola, I think there would be more difficulty in melting the very light grade of steel scrap such as was used in the runs given than the heavier stock, and in all these experiments, we used nothing but very low grades of material, some of them running only 75 or 80 per cent. Fe. The cast-iron borings and the lightest grade of scrap, such as we used, usually go to the blast furnace.

In making a fairly extensive survey of power, if there is a big tonnage of iron to melt power can be obtained a good deal under one cent in all districts where coal is fairly cheap. For instance, in one operation we are buying about 10,000 kw., not on the pig iron but in another operation, under conditions where they have the right to shut us off if they need the power. You can operate under such conditions if you are making pig iron. When you are handling steel scrap into direct castings you can

afford to pay more for the power in order to have it in the daytime when you want it; for instance, if you are in motor-car service.

T. L. JOSEPH, Minneapolis, Minn.—Did Mr. Baily water-cool the bottom of his furnace?

T. F. BAILY.—The furnace bottom was not water-cooled, although the bottom electrode was water-cooled.

R. M. KEENEY, Hartford, Conn. (written discussion).—Mr. Baily has always been a pioneer in the application of electric heating to industry, and our practice in the electrical heat treatment of metals and alloys really dates back to the carbon resistance furnace developed by Mr. Baily and publicly demonstrated for the first time at an exposition held in Pittsburgh in 1913.

The experiments described are of particular interest because the fundamental basis of carbonization in the blast furnace is applied to the electric furnace; namely, the steel scrap is melted or partly melted above an incandescent bed of coke through which it and the slag pass, absorbing carbon and sulfur. Arriving at the base of the column of coke, the molten steel, now cast iron, drops through an enveloping layer of basic slag, where sulfur is removed. The method, if it is workable from a furnace-operating standpoint, appears to have possibilities of application under three conditions:

1. For production of pig iron in localities where there is an excess of steel scrap available and where dump power can be obtained at a low price. However, for synthetic production of pig iron from scrap, the process would be subject to fluctuating local economic conditions such as depletion of the supply of scrap and loss of the source of dump power caused by the demand of other local industries able to pay a higher price.

2. For production of gray-iron castings in the foundry operated as an adjunct to a metal-working concern which has a constantly increasing supply of skeleton steel scrap, turnings or forge flashings for which only a low price is paid by the scrap dealer.

3. For the production of foundry iron from sponge iron.

Mr. Baily's experiments were conducted on a comparatively large scale in an 800-kw. furnace, producing about one ton per hour. A number of questions arise regarding operation which are not covered in the paper:

1. Is the coke column maintained by accumulation from the coke charged with the scrap or is it necessary to directly replace it from time to time?

2. What lining material was used for hearth and sides of the furnace?

3. What refractory was used for the roof, and how many hours of operating life were obtained per roof? With the method of operation described one might expect difficulty in maintenance of the roof.

4. Were the electrodes regulated by hand or with a regulator, or was there no electrode regulation, the load on the furnace being kept constant by voltage regulation?

5. At what voltage was the furnace operated?

6. What were the main difficulties of operation and was there any difficulty caused by formation of calcium carbide with a resulting slowing up of the furnace?

As to whether this process can be considered for the average foundry depends wholly on the local economic situation. In the average foundry located in a center of surplus steel scrap, I believe a duplex process might prove more economical unless a very cheap power supply is available. By a duplex process I mean:

1. Carbonize steel scrap in an electric furnace of the shaft type, making no attempt to remove sulfur or control the silicon and manganese.

2. Desulfurize and make silicon and manganese additions with ferroalloys in a refining furnace directly charged by tapping from the shaft furnace.

The duplex method should result in a considerable saving in power consumption, and it would not be unreasonable to expect as low a figure as 500 kw.-hr. per ton in the shaft furnace and not over 100 kw.-hr. per ton in the desulfurizing furnace, the figure given by Dr. Moldenke in his paper on duplexing,[1] provided that silica and manganese were added as ferroalloys. This total for the two steps, 600 kw.-hr., is 20 per cent. lower than Mr. Baily's estimated consumption of 750 kw.-hr. per ton. With the prevailing cost of power in industrial centers, reduction of silica is rather expensive. The most efficient ferrosilicon furnaces use about 5 kw.-hr. per pound of silicon. If silicon is to be raised 2 per cent. over that in the steel scrap, 40 lb. of silicon per ton must be reduced, consuming 200 kw.-hr., which with power at 1.5 c. per kilowatt means a cost of $3 per ton of iron for power. In a synthetic pig-iron furnace, of a size practical in the average foundry, there would probably be a consumption of 300 kw.-hr., or a cost of $4.50 per ton of iron. The silicon required can be furnished as ferrosilicon for $3.

Today many factories throughout the East are investigating the electric furnace as a means of production of special grades of gray iron and as a means of utilization of light steel scrap. There is considerable indecision as to whether basic or acid operation should be used and as to whether straight electric melting or duplexing after the cupola should be practiced. In two cases which I have investigated during the past month, synthetic gray iron can be produced in the basic electric furnace at a slightly lower cost than the present cupola iron, because of the low-priced charge available.

T. F. BAILY.—As to the coke additions, they were made along with the rest of the charge so as to maintain the coke column at about the same height all the time. In other words, if we charged 1000 lb. of steel scrap we charged 100 lb. of coke, so as to keep the bed of coke about the same height.

The furnace was lined throughout with a standard type of high-alumina brick running about 70 per cent. Al_2O_3.

The life of the roofs in a commercial furnace should be very long, for there is always a condition of melt-down, so that the roofs are not punished. In other words, probably there will never be over one-half hour's supply of unmelted steel in the furnace before tapping, therefore there is not the condition there would be in an electric melting and refining furnace, where refining is carried on for the last hour or two and where the furnace is at full temperature and the roof is being severely punished. As a matter of fact, the roofs in these furnaces seldom run over about 1800° F., on account of the cold material that is always coming in.

The electrode regulation was both hand operation and some old-type Thury regulators that happened to be available. As a matter of fact, after 15 runs we had so much trouble with the Thury regulators that we regulated entirely by hand. A man would go over every 15 min. to the meters to see that all the electrodes were pulling uniformly. Regulation was by movement of the electrodes rather than by a change of the voltage.

The electrodes, all the time, were playing on the coke instead of arcing from a so-called bath, as in an ordinary steel furnace, and through the bath to the other electrodes they arced on the coke and then carried through the coke as a resistance unit, so that there was no tendency to surge.

The voltage was 110 volts. At times it ran as high as 200 volts, but that was too high a voltage for the small furnace we had, which was only 5 ft. in outside diameter.

[1] R. Moldenke: The Electric Furnace in the Iron Foundry. *Trans.* A. I. M. E. (1922) **67**, 544.

As to furnace difficulties on the small units, we froze it up two or three times, possibly because we were operating all these runs in the winter, when the weather frequently was 10° below zero, and at that time we ran only 10 hr. a day. When we went on 24-hr. operation, we had no trouble with heats hung, or on the inside of the furnace.

We did not see any carbide. Our temperature never was high enough to reach a calcium carbide condition. Our ordinary tap condition was around 2650° F. and our slags showed no calcium carbide.

With regard to the duplex method, I think the best way, especially in competition with blast-furnace iron, is to use a rotary preheater or melter and run the charge with the slag additions having been melted down along with the scrap in the electric furnace and the silicon and manganese reduction carried on there.

G. B. WATERHOUSE, Cambridge, Mass.—Mr. Williams has been on the Pacific Coast, where conditions are said to be favorable for scrap.

T. F. BAILY.— A survey on the Coast brought out the fact that there is not a great deal of scrap.

C. E. WILLIAMS, Columbus, Ohio.—I think Mr. Baily is right in his statement that there is not a great deal of scrap on the Pacific Coast. I believe that the present annual supply is 350,000 tons a year. Of course, the supply of steel scrap depends upon economic conditions and as the price paid for scrap increases a larger tonnage becomes available, because it can be shipped from greater distances. This tonnage of steel scrap is consumed by the steel industry on the Pacific Coast. However, there, as in other parts of the country, there is a sizable tonnage of light scrap not well suited for open-hearth practice but satisfactory for use in electric melting operations such as the one described by Mr. Baily.

At one time scrap was plentiful and cheap on the Pacific Coast, the open-hearth steel practice being based almost entirely on the use of steel scrap. As the output of steel increased the supply of scrap became inadequate and the price soon reached a point where it could not be considered cheap. From that point on, any further increase of the steelmaking capacity was necessarily based on the use of pig iron, and thus the production of pig iron in Utah became possible.

The price of steel scrap in any locality remains at a certain percentage of the price of pig iron and the amount of scrap that is used in the open hearth is dependent on economic conditions—the price of scrap, the price of pig iron, etc.

On the Coast, as long as there was an abundance of scrap at a price that was low compared to the price of pig iron, the maximum amount of scrap, about 90 per cent., was used in the open hearth. Then, as the production of steel increased, the price of pig iron and scrap began to approach each other until at present the situation is not unlike that in some parts of the East. However, there is a supply of scrap available on the Pacific Coast for a small foundry operation, just as there is in almost any district in the United States where there are manufacturing enterprises that produce scrap which is not desired for steel melting.

When, after the war, we looked into the possibility of making synthetic cast iron from these light and cheap grades of scrap, the price of pig iron on the Pacific Coast was high because the blast-furnace operation had not yet started in Utah, and conditions in the iron and steel industry had not settled down to the point where cheap pig iron was available. The production of synthetic cast iron, or even of pig iron, from cheap grades of scrap appeared feasible.

By the time we had worked out the fundamental factors on which the introduction of sufficient carbon depended, conditions had changed and the production of pig iron from scrap was out of the question, even though power could be obtained for

less than ½ c. per kw-hr., and scrap could be obtained for around $10 a ton. I do not believe that more favorable conditions than these now exist in other centers using cast iron.

We found that during the war producers of synthetic cast iron from steel scrap had not been able to increase the carbon to much above 3 per cent. without destruction to the roof of the furnace. Our investigation developed means whereby the carbon content could be raised without difficulty to the figures Mr. Baily obtained.

These conditions were, principally, the use of a coke as free from ash as possible, such as a petroleum coke, and the absence of slag in the bath of metal. The work was carried on in a jobbing foundry using a 1½-ton electric furnace. During these experiments, which were continued for over a year, four heats were made each day for six days a week. Sometimes two heats of iron and two of steel for castings were made in a day and sometimes one of iron and three of steel. During that year's operation, we were able to obtain some fairly accurate cost data under what might be considered commercial conditions. The furnace was not well insulated and was not powered sufficiently, having about 600 kw. input. Under these conditions the power consumption was about 650 kw-hr. per ton. Undoubtedly, with a larger modern furnace, a power consumption of 450 to 550 kw-hr. per ton would have been possible.

In this work it was shown that the carbon contents could be raised to as high a point as desired up to 4 per cent., by holding the heat for 1½ hr. after melting. A 3-hr. period from tap to tap was possible in making a product containing about 3.25 per cent. carbon, the carbon content required for ordinary iron castings. The silicon content was adjusted by the addition of ferrosilicon. An acid-lined furnace was used. The use of steel scrap, which is low in sulfur and in phosphorus and of about the right manganese content for cast iron, made necessary only the adjustment of the desired silicon content.

Assuming that an iron containing 2 per cent. silicon is made, the cost of silicon added as ferrosilicon is about $3 per ton. Mr. Baily said that in his work about 300 kw-hr. would be required for introducing the silicon and manganese. With power costing 1 c. per kw-hr., the power cost per ton would be about $3.

Taking into account the power consumed in the reduction of silicon, Mr. Baily's work shows about the same power consumption to produce 1 ton of iron as ours did. Evidently the costs of the two operations would be similar. Therefore, I do not see any advantage in using the unusual type of furnace or the new method of introducing silicon and manganese over the use of a standard furnace and usual methods for the introduction of metalloids.

The question of the production of cast iron from steel scrap is now an economic one. The metallurgical operations are defined. Commercial equipment and ordinary practice can be used successfully. Commercial feasibility depends upon the costs of raw materials and power and upon the quality of product to be made.

Reclaiming Steel-foundry Sands

By A. H. Dierker,* Columbus, Ohio

Next to the metal itself, molding sand is the most important raw material used in the manufacture of steel castings. There are no accurate figures available but probably it would be safe to say that the average steel foundry uses approximately 1000 lb. of new molding sand per ton of castings produced. With untreated sands costing from two to four dollars (in some extreme cases it may run as high as eight or ten dollars) per ton delivered at the foundry siding, molding sand is an important item in the cost of making castings, and any information that may help to reduce this sand consumption should be of interest to the industry.

Fundamental Considerations

In a general way, molding sand in the average steel foundry passes through the cycle shown in Fig. 1. This diagram indicates that if all
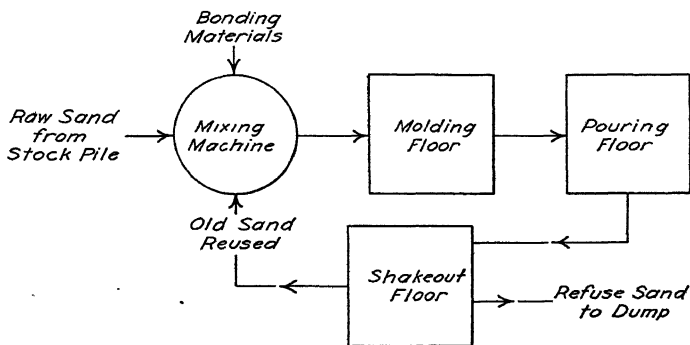
Fig. 1.—Movement of molding sand in the average steel foundry.

of the sand could be returned from the shakeout floor to the mixer no new sand would be required from the stock pile and molding costs would be reduced accordingly. Unfortunately, for reasons to be discussed later, it has heretofore been necessary to dilute the used sand constantly with new raw sand in order to maintain the properties that are essential to the production of satisfactory molds.

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To prevent an accumulation of sand in the foundry it has been neces-
sary to waste used sand in amount equal to the new sand added.   To
most foundries, wasting this sand is an added expense.   If it were possible
to treat the used sand so as to maintain the desired properties, the only
new sand required would be that necessary to replace the sand lost in
the treating process and in the cleaning room, which raises the question
Can this be done; and, if so, how?   This paper covers a series of investi-
gations made to determine:

1. What causes molding sand to lose its desirable properties.

2. How these properties can be maintained or restored without the
use of new sand.

COMPOSITION OF SANDS FOR MOLDING STEEL

Molding sands (in this paper this term will be used to include core
sands as well) are an aggregate of silica sand bonded with some plastic
material (green binder) and, in the case of sand for dry sand molds and
cores, an additional dry binder.   The sand grains are quartz of a fairly
uniform size and in ·most steel-foundry sands most of the grains are
between 40 and 70 mesh.

Numerous materials are used in bonding these sands, but in general
they can be divided into two classes:

1. *Green Binders.*—These are usually a plastic colloidal material
and give the sand plastic properties when mixed with the proper amount
of water.   Those most widely used are fireclays, including bentonite,
and "corn" flour.   Corn flour is a partially dextrinized starch made
from corn.

2. *Dry Binders.*—These give the sand its maximum strength after it
has been dried or baked.   The more common dry binders are linseed
oil, pitch, rosin, water-soluble binders such as dextrine, molasses, etc.,
and numerous trade-marked oils and compounds.

Most steel-foundry sands used in this country are of the synthetic
type; *i. e.*, a quartz sand containing little or no bonding material is mixed
in a suitable machine (usually a mill of the muller type, a modified dry
pan) with the proper amount of binders to form a plastic mixture suit-
able for molding or core work.

DETERIORATION OF MOLDING SANDS IN USE

What happens to sand that comes in contact with molten steel was
strikingly shown by the following simple experiment.   A hole was cut
through the top of a large mold previous to pouring.   The mold was then
poured and, as the steel rose in the mold, a few small grains of sand were
dropped on its surface.   There was an immediate reaction of the sand
with the film on the surface of the metal, forming a slag which remained
liquid after the metal had solidified.   Since the freezing point of steel

is below the melting point of silica or the silica-alumina eutectic, it can be seen that another flux has been introduced to react with the sand to form a low melting slag. As will be shown, the surface of the steel appears to be oxidized to a ferrous condition which readily reacts with the silica sand.

A number of small castings, simple blocks of steel 2 by 8 by 8 in., weighing about 37 lb. each, were poured in molds made of various sand mixtures, using dried Ottawa sand as a base. A sample of the scale formed at the contact of the steel with the sand was obtained and scraped as clean as possible from adhering sand. An analysis of this scale gave the results shown in Table 1, which show that pouring steel into sand

TABLE 1.—*Chemical Composition of Scale Formed at the Mold Face*[a]

Composition of Sand Mixture	Analysis of Scale			
	FeO, Per Cent.	Fe₂O₃, Per Cent.	MnO, Per Cent.	Fe, Per Cent.
1. Sand, 94.5 per cent............ ⎫ Clay,[b] 5.5 per cent............. ⎬	12.86	4.58	0.64	13.20

2. Sand, 93.2 per cent............ ⎫
   Clay, 5.5 per cent.............. ⎬
   Pitch, 1.3 per cent............. ⎭
	17:69	0.36	0.36	14.00

3. Sand, 89.0 per cent............ ⎫
   Clay, 5.5 per cent.............. ⎪
   Pitch, 1.3 per cent............. ⎬
   Silica wash,[c] 4.2 per cent........ ⎭
	15.41	0.60	0.45	12.40

4. Sand, 98.8 per cent............ ⎫ Corn flour, 1.2 per cent......... ⎬	17.23	0.40	0.50	13.68

5. Sand, 94.5 per cent............ ⎫
   Corn flour, 1.3 per cent......... ⎬
   Silica wash[c], 4.2 per cent....... ⎭
	· 14.14	2.87	2.01	13.00

[a] It is very difficult to get comparative samples of scale, and the results, as a consequence, are not exactly comparable. They do, however, prove the point in question; namely, that the surface of the metal is oxidized, chiefly in the ferrous state; that the ferrous oxide is absorbed by the sand.
    The scale, when crushed to a fine powder, had the characteristic green color of a ferrous silicate.
   [b] Analysis of the clay used was as follows: SiO₂, 59.80 per cent.; Al₂O₃, 24.91; Fe₂O₃, 0.47; FeO, 0.72; CaO, 0.56; MgO, 0.51; Na₂O, 1.43; K₂O, 1.20; TiO₂, 1.40; Ignition loss, 9.20.
   [c] 200-mesh pulverized quartz.

molds introduces ferrous silicates into the sand and that these, although small in amount for one pour, would accumulate rapidly were the sand continuously reused.

EFFECT OF TEMPERATURE ON SAND

Immediately back of the mold face the sand is subjected to comparatively high temperatures, which vary with the distance from the mold face and the size of the casting. For the purposes of this investigation it was necessary to know, approximately at least, the value of these tem-
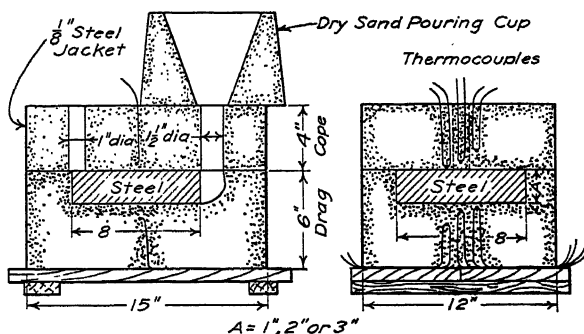
FIG. 2.—ARRANGEMENT OF THERMOCOUPLES IN MOLD FOR TAKING TEMPERATURE OF THE SAND.
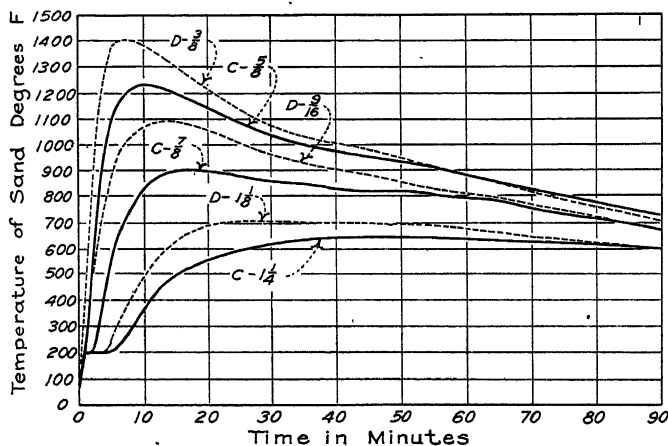
FIG. 3.—TEMPERATURE OF SAND AT VARIOUS TIMES AFTER POURING.

C and D indicate cope or drag. Figures following these letters give distance from the metal in inches.

Size of casting, $1 \times 8 \times 8$ in.

Approximate pouring temperature, 2750° F.

Sand mixture: Ottawa sand, 88 per cent.; fireclay, 12; moisture, 3.50.

peratures. For this reason, a brief investigation was made to determine the maximum temperature reached by sand in various parts of a mold in which steel had been poured.

Iron constantan thermocouples of No. 16 gage wire were rammed in a mold, as shown in Fig. 2. An attempt was made to keep the couple nearest the hot metal far enough from the mold face so that it would not

be subjected to a temperature above 1500° F. The couples were moved during the ramming operation and it was found that the only reliable means of determining their location was to place them in approximately the position desired and wait until the mold had been poured and readings
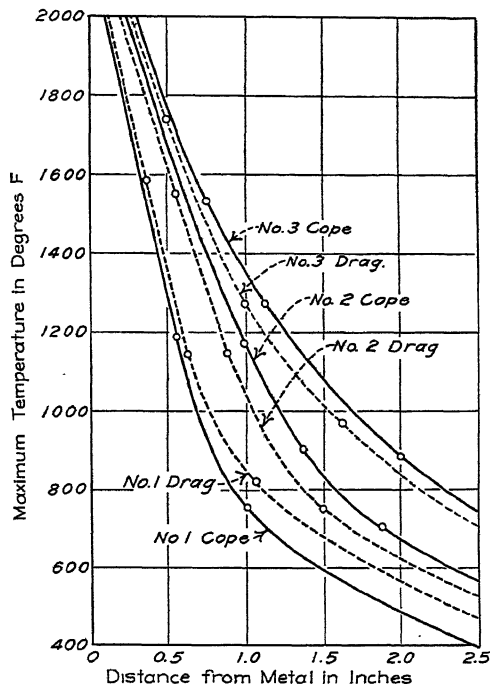
Fig. 4.—Maximum temperature reached by sand in molds for castings of various thicknesses.

Specimen Number	Size of Casting, Inches	Sand Mixture, Per Cent.		
		Ottawa Sand	Fireclay	Moisture
1	1 × 8 × 8	94	6	2.66
2	2 × 8 × 8	94	6	2.80
3	3 × 8 × 8	94	6	Dried

Approximate pouring temperature, 2750° F.

taken; then, by carefully picking the mold to pieces, the couples could be located and their distance from the metal could be measured.

Readings were taken on an indicating potentiometer connected to the various couples through a multiple switch. It required only about 30 sec. to get the readings of the six or seven couples.

Fig. 3 gives a typical time-temperature curve for one of the tests. Fig. 4 gives the maximum temperature curves for the three sizes of castings tested.

Distance from mold face, kind and size of flask used, temperature of metal, kind of sand and moisture content, and shape of casting are all factors which influence the maximum temperature reached in various parts of the mold. A complete investigation of mold temperatures would of necessity take these variables into consideration. The data we have secured, although incomplete, are sufficient for the purpose of this paper. A study of Fig. 4 reveals that the temperature reached by the bulk of the sand is surprisingly low. This is fortunate, as it simplifies our problem somewhat.

In studying the effect of temperature on molding sand it is well to keep in mind that such sand is composed of two distinct constituents; i. e., the quartz grains and the binding material used to hold these grains together and give the sand its plastic properties. We will consider the binders first.

EFFECT OF TEMPERATURE ON BINDERS

Fireclay.—Value of clay as a green binder lies in its colloidal properties. At higher temperatures the water of hydration is driven off and the colloidal properties are permanently destroyed. The clay used in this investigation loses its combined water markedly at 930° F. and is completely dehydrated at 1400° F. The clay at the mold face may be hard-burned. However, most of the clay that is affected by the temperature at all is simply dehydrated and occurs in used sand either free or entrapped by the other binders in a coating on the sand grains.

Organic Binders.—These are the oils, starches (farinaceous or paste binders), and water-soluble materials (molasses, dextrine, and sulfite pitch). They are burned out completely near the mold face but further away are merely charred and still further away are unaffected and remain as coatings on the sand grains.

Pitch.—When pitch is heated, the volatile matter is driven off, leaving a cokelike carbonaceous material. This coke is burned off only at a high temperature. In actual practice, the pitch is completely burned only from that sand which is within about ½ in. of the mold face. Most of the pitch remains as a firm coating on the sand grains. Thus, in used molding sand, the quartz grains are surrounded by the different binders in various stages of oxidation and decomposition and a small amount of ferrous silicates from the mold face.

SIGNIFICANCE OF CHANGES IN SAND MIXTURE

A representative sample of used sand was secured and a wet screen analysis made of it (see Fig. 5). Wet screening was necessary because in dry screening the peculiar carbonaceous fine material sticks to the screen meshes.

A microscopic examination of this sand showed practically all of the grains completely coated with binding materials, especially the cokelike pitch residue.   This sand was then put in a No. 0 Simpson foundry mixer
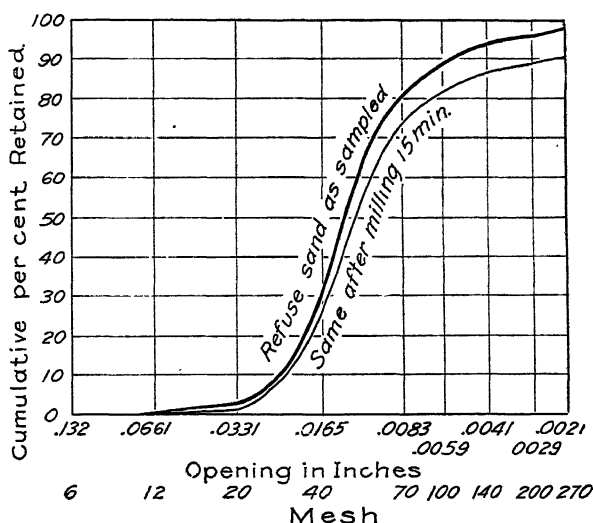
FIG. 5.—WET SCREEN ANALYSIS OF REFUSE SAND BEFORE AND AFTER MILLING.

(a modified form of the dry pan) and milled for 15 min.   A screen analysis of the sand was made (see Fig. 5) and the particles retained on the different meshes were examined microscopically.   That retained on the 12-mesh and 20-mesh screens proved to be large irregular opaque grains,
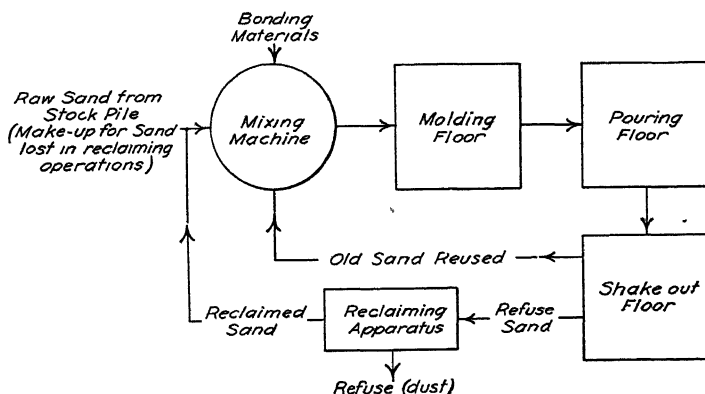
FIG. 6.—MOVEMENT OF SAND IN A FOUNDRY AFTER INSTALLATION OF RECLAIMING APPARATUS.

apparently partly fused lumps of clay.   From 20 to 100 mesh, which included the bulk of the material, the sand consisted almost entirely of clean silica grains.   From 140 mesh on, increasing amounts of opaque

grains were present which were either some dark-colored mineral or melted pitch, or both.

The dry density of the sand before milling was 1.316 g. per c.c.; after milling it was 1.667 g. per c.c.; a 27 per cent. increase. This indicates that in milling used sand the coating is broken from the sand grains and ground to a fine powder which fills in the interstices between the sand grains.

If this unmilled refuse sand is to be used as it is, or with merely the free dust removed, it must first be rebonded. If the sand is rebonded in such a way that the coatings on the sand grains remain intact, the binder adheres to the coating and not to the sand grain itself; thus, in subsequent ramming operations, much of the sand-grain coating will be broken, especially adjacent to the pattern, releasing unbonded grains which may cause considerable trouble. On the other hand, if the sand is mixed intensively, as is usually the case where a pan mill is used, a large volume of free powdery material is formed, which not only fills up the interstices, decreasing the permeability, but also, because of its large surface area, absorbs a great amount of binder, making the use of an excessive amount of that material necessary.

Effective Reclaiming

The foregoing facts show that merely removing the loose fine material from used sand is not sufficient, and that effective reclaiming involves two essential steps: (1) breaking the coating of foreign material from the sand grains; (2) separating this foreign material from the good sand.

If the sand were treated in this way, there would remain, as good sand, comparatively clean quartz grains, which could be charged into the mixing machine as a substitute for new sand in the making of molding-sand mixtures. The cycle followed by the sand in the foundry would then be as shown in Fig. 6. It will be noted that, in this cycle, only the sand formerly discarded as refuse is treated in the reclaiming apparatus. Treating all of the sand before re-use would involve, in most cases, the handling of excessive tonnages and would mean unnecessary expense.

This theory of reclaiming is based on the assumption that there is no appreciable deterioration of the quartz grains themselves. However, there seemed to be some question of the validity of this assumption. Muntz and Roubien[1] doubt the advisability of using old sand in facings for steel castings. They state that "under repeated heatings to high temperatures, the quartz in the sand undergoes two changes: (1) A number of particles are broken up, resulting in easily fused sharp edges and also in smaller grains; (2) such particles as are not broken up increase very rapidly in volume to the extent of 20 per cent. after a short time."

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[1] G. Muntz and E. Roubien: Study of the Steel Foundry Sand Problem. *Foundry* (1917) **45**, 315.

To clear up this point, an investigation was made of the durability of molding-sand grains under repeated heatings.

STABILITY RELATIONS OF SILICA

Silica (SiO_2) can form three different crystalline minerals—quartz, tridymite and cristobalite. Quartz is the form in which silica is usually found in nature; the others are of rarer occurrence.

At temperatures up to 575° C. (1067° F.) an inversion takes place, the quartz changing from the alpha to the beta phase. This inversion takes place rapidly, being practically instantaneous. At 870° C. (1598° F.) beta quartz is no longer stable, tridymite being the stable form of SiO_2. However, this inversion, in the absence of a flux, apparently does
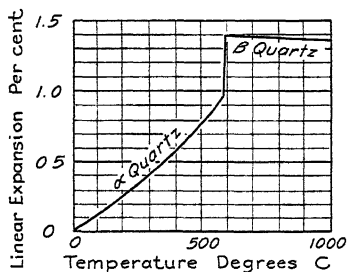
FIG. 7.—LINEAR EXPANSION OF
QUARTZ (McDOWELL).
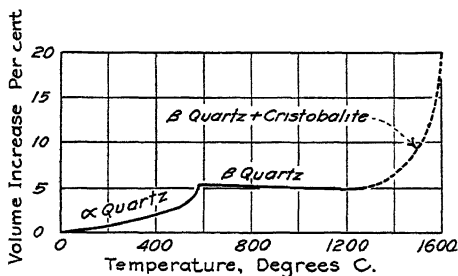
FIG. 8.—VOLUME INCREASE OF QUARTZ
(McDOWELL).

not take place and even in the presence of a flux takes place very slowly. At 1250° C. (2282° F.) cristobalite is the stable phase and the beta quartz inverts to cristobalite. At this temperature, the inversion is extremely sluggish, Fenner[2] finding that 108 hr. heating produced only a small quantity of cristobalite. At higher temperatures the velocity of inversion increases, and, according to Fenner, is fairly complete in one hour at 1570° C. (2858° F.).

These different inversions are accompanied by volume changes. Fig. 7 shows the linear expansion of quartz according to LeChatelier, while the volume increase as determined by the Geophysical Laboratory is shown in Fig. 8.[3]

The alpha to beta inversion of the quartz is reversible; the alpha phase exists only below 575° C. (1067° F.) while the beta phase exists only above that temperature. The inversion to cristobalite is apparently permanent and the silica does not revert to quartz on cooling.

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[2] C. N. Fenner: Stability Relations of Silica Minerals. *Amer. Jnl. Sci.* [4] (1913) **36**, 383.

[3] Figs. 7 and 8 are taken from J. Spotts McDowell: A Study of the Silica Refractories. *Trans.* A. I. M. E. (1917) **57**, 46.

PRACTICAL CONSIDERATIONS

The temperature reached by sand grains in a mold depends on their distance from the metal and on the temperature and thickness of the metal itself. From the results of experiments on mold temperatures, the author feels certain that, in castings of which the sections do not exceed 1 in., only the grains within less than $\frac{1}{8}$ in. of the metal reach a temperature above 1400° C. (2552° F.). In the average mold this would represent less than 1 per cent. of the sand. Since the beta quartz to cristobalite inversion will not take place with any appreciable speed below this temperature, we can dismiss this inversion as a factor of any importance in the disintegration of molding-sand grains. Between 575° C. (1067° F.) and 1250° C. (2282° F.) there is practically no volume change in the quartz and it is only the temperature up to and through 575° C. (1067° F.) that we need consider.

Day, Sosman, and Hostetter[4] found that quartz has a strong tendency to crack at the inversion temperature; i. e., 575° C. (1067° F.). Wright and Larsen[5] say. "The fact that thin plates of quartz may warp and bend temporarily at the inversion temperature, thus finding relief from the strains set up on the change, while thicker plates bend less easily and tend to fracture more readily, is a factor which should be considered in any particular case. Small grains being thus less liable to fracture may not show the phenomena of shattering as clearly as might be expected."

It can be seen, therefore, that the size of the grain must be taken into consideration and the author's investigation has attempted to determine whether sand grains of the size usually found in steel-molding sands will be affected by repeated heating through the inversion point.

TYPES OF SAND GRAINS

Practically all steel-molding sands are obtained from sandstone deposits and the size and shape of the grains depend on the nature of their deposition. The grains of water-laid sands are irregular and more or less angular in shape; those of the eolian or wind-blown sands, due to abrasion during transportation, are rounded and the larger grains approach a sphere in shape. In the quartzites, the grains, due to metamorphism, have been consolidated into a more or less solid mass of quartz.

In mining molding sands from sandstones, a weakly cemented sand is usually selected, which breaks down readily and in which the original shape of the grains is retained. If quartzite is used, it must be crushed and screened, and the resulting grains are angular, with very sharp edges.

    [4] A. L. Day, R. B. Sosman and J. C. Hostetter: Determination of Mineral and Rock Densities at High Temperatures. *Amer. Jnl. Sci.* [4] (1914) **37**, 1.

    [5] F. E. Wright and E. S. Larsen: Quartz as a Geologic Thermometer. *Amer. Jnl. Sci.* [4] (1909) **27**, 438.

TABLE 2.—*Screen Analysis of Quartz Sands Tested for Durability*

Sand	Mesh	Mesh No.	Opening Mm.	Cumulative Per Cent. Retained								
				Not Milled			Milled 15 Minutes			Milled 45 Minutes		
				Washed	Heated	Quenched	Washed	Heated	Quenched	Washed	Heated	Quenched
Ottawa, Ill.	20	5.0	0.833	0.0	0.10	0.0	0.0	0.06	0.0	0.0	0.0	0.0
	28	4.5	0.589	4.45	5.38	4.15	3.64	3.46	1.39[a]	2.88	1.32	0.31
	40	4.0	0.420	30.90	34.15	30.25	26.85	25.13	12.43[a]	19.59	11.20	3.42
	48	3.5	0.295	74.15	77.18	71.52	64.16	61.18	41.57[a]	49.57	38.38	18.24
	70	3.0	0.210	88.60	92.58	87.28	81.49	80.13	63.16[a]	66.39	59.90	35.72
	100	2.5	0.149	94.41	97.95	94.31	90.40	89.33	77.23[a]	78.08	74.30	56.01
	140	2.0	0.105	97.61	99.24	97.72	94.93	93.29	87.22[a]	85.20	82.65	71.05
	200	1.5	0.074	98.44	99.40	98.58	95.83	94.40	90.91[a]	87.86	85.84	77.88
	270	1.0	0.053	99.05	99.52	99.35	97.27	95.41	94.16[a]	90.98	89.11	85.01
	−270	0		100.00	100.00	100.00	100.00	100.00	100.00[a]	100.00	100.00	100.00
Jackson, Ohio	20	5.0		0.0	0.10		0.04	0.05		0.08	0.0	
	28	4.5		0.08	2.61		0.94	1.21		0.39	0.37	
	40	4.0		2.20	16.54		9.12	10.54		3.17	3.38	
	48	3.5		14.74	77.07		52.08	59.05		27.12	29.45	
	70	3.0		73.60	91.97		74.98	79.60		51.82	54.83	
	100	2.5		90.92	96.58		84.56	88.90		65.73	70.06	
	140	2.0		95.34	98.92		91.39	93.84		77.62	80.44	
	200	1.5		98.23	99.26		93.76	95.41		82.31	84.08	
	270	1.0		99.45	99.41		95.02	96.83		87.20	88.92	
	−270	0		100.00	100.00		100.00	100.00		100.00	100.00	
Crushed quartzite	20	5.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	28	4.5		0.11	0.12	0.07	0.0	0.0	0.0	0.0	0.0	0.0
	40	4.0		0.87	1.05	0.71	0.30	0.21	0.15	0.13		
	48	3.5		34.80	32.00	34.46	25.42	23.36	18.20	16.08	11.04	4.72
	70	3.0		83.67	81.94	79.96	71.17	68.86	61.59	53.49	43.77	29.63
	100	2.5		97.06	96.29	95.91	87.88	87.16	82.14	73.27	68.50	53.95
	140	2.0		99.15	99.17	99.08	93.59	93.29	90.11	83.36	80.74	71.32
	200	1.5		99.63	99.72	99.58	95.15	95.06	93.08	86.82	85.25	78.31
	270	1.0		99.92	99.95	99.88	98.57	96.17	95.16	90.33	88.68	84.79
	−270	0		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

[a] Milled 25 minutes.

In the author's investigation a sample of each of the following sands was used: (1) sand from the St. Peter's sandstone of Ottawa, Ill., which is a wind-blown sand; (2) a sample from the Pottsville formation near Jackson, Ohio, which is a water-laid sand; (3) crushed and screened quartzite used ordinarily as a glass sand.

The Ottawa and Jackson sands were washed free from clay substance, by the standard A. F. A. method, before testing. The crushed quartzite was used as received.

In Table 2, the samples marked "heated" were treated in the following manner: A nickel tray was kept in an electric resistance furnace which was maintained at a temperature of 1200° to 1250° F. The sand samples were poured on to this tray and kept in the furnace for 5 min. They were then removed and poured on to a steel pan $\frac{1}{64}$ in. thick, which was kept floating on cold water. After cooling the sand was poured back on to the nickel tray, which had been kept in the furnace, and the process was repeated. In this manner the sand was heated and cooled rapidly through the alpha-beta inversion point (1067° F.). Each sample was run through this heating and cooling cycle eight times.

The samples marked "quenched" were heated, in nickel crucible, to 1500° F. and then poured in cold water.

All screen analyses were made by running 15 min. in the Ro-Tap machine.

After the eight heatings the sand samples were milled in a small ball mill 3 in. dia. by 3 in. long, made of casehardened steel. The mill was loaded with twenty-five $\frac{3}{4}$-in. balls and was rotated at 40 r.p.m. for the times indicated.

In screening on the Ro-Tap machine, much of the fine material (-270 mesh) sifts out through the joints between the screens and is lost; for this reason, the amount of -270 material was, in each case, obtained by difference.

MICROSCOPIC EXAMINATION

The larger grains of Ottawa sand are rounded and almost spherical in shape; the smaller grains are more irregular but the edges are more or less rounded; some of the grains show small cracks; all of them are transparent. After being heated and cooled through the inversion point eight times the grains show little change. A few more appear to be cracked but not enough more to be certain on this point. The grains of the sand that had been heated and quenched showed distinct signs of disintegration; a few of the grains had been shattered and many were badly cracked. However, about one-half of the grains showed no signs of injury. After milling 45 min., the larger grains remaining were those that were practically free from cracks.

The grains of the Jackson sand are irregular with different degrees of angularity. Many of the grains are partly or wholly opalescent. Repeated heating through the inversion point seemed to increase this opalescence. However, milling tests indicate that this quality does not necessarily mean a weakness in the grains.

The quartzite consists of uniformly sized grains, angular and with sharp edges. The majority of grains are clear but a few are opalescent. As in Jackson sand, this opalescence is increased on repeated heating through the inversion point but this heating does not seem to affect the grains in any other way. Quenching did not seem to crack this sand as badly as the Ottawa sand, which was probably due to its normally smaller grain size, but quenching did increase the opalescence or translucency of the grains. About 75 per cent. of the grains of the quenched sand exhibited this phenomenon.

If heating through the inversion point sets up internal stresses in the grains which are not relieved by cracking, such grains should show undulatory extinction when examined with a polarizing microscope using crossed nicols. The samples were examined for this property and although some grains in the raw sand showed undulatory extinction the number was apparently not increased by the repeated heating through the inversion point. It must be borne in mind that the majority of sand grains were formed originally by crystallization from molten magmas and that in cooling these grains pass through the several inversion points. Grains formed in this manner exhibit the characteristic properties of quartz that has been heated and cooled through the inversion points.

From the results of this phase of the investigation, the conclusion would be justified that the resistance to disintegration of quartz grains of a size usually found in steel-molding sands is not lessened by a fairly rapid heating and cooling through the alpha-beta inversion point; i. e., 575° C.

Our samples were cooled at a much more rapid rate than would ordinarily be the case in actual foundry practice. However, even in the case of the quenched samples, which is a much more severe treatment than the sands would ever receive in regular use, the grains are not disintegrated to a point where the reclaiming of the good portion would be unprofitable.

The results of the milling tests check fairly closely with what one would expect after a microscopic examination and the milling test should give a good indication of how the sand grains will stand up under the milling and ramming received in the foundry. The rounded grains of Ottawa sand are most resistant to the action of the mill. The sharp edges are readily broken from the angular sands by the action of the balls and the larger grains rounded. After being rounded, these grains should be, and apparently are, as resistant to disintegration as the naturally rounded grains.

From observations in the foundry, it appears that only the grains that come in contact with the metal are broken up to any noticeable extent. Since these grains absorb ferrous iron their disintegration is desirable, for the resulting small particles would then be removed in the cleaning operation and the ferrous iron content of the sand kept at a low point.

APPARATUS FOR RECLAIMING

After trying out, on a small scale, several types of reclaiming apparatus it was found that the combination of a muller-type sand mill and an air classifier followed by a dust collector gave the best results.
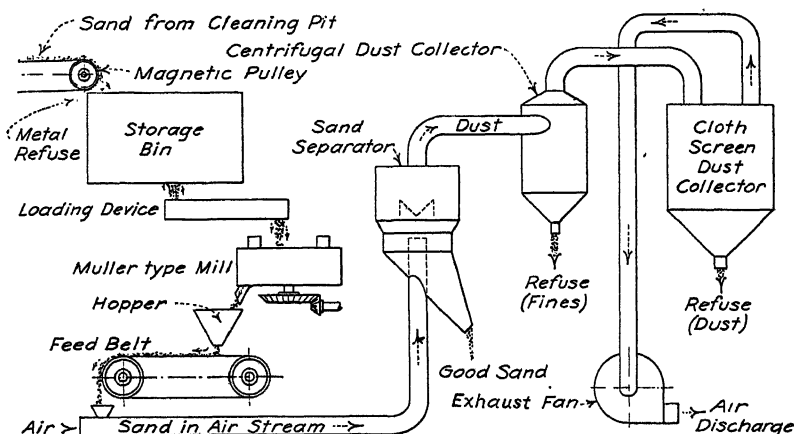
FIG. 9.—SCHEMATIC DIAGRAM OF SAND-RECLAIMING PLANT.

Results from an experimental unit indicated that a recovery of more than 70 per cent. could be attained and that the reclaiming of refuse sand should prove highly profitable. On the basis of these tests a full-size unit was designed and installed. The schematic diagram shown on Fig. 9 should give a clear idea of the type of apparatus used and method of operation. There are, of course, details that contribute to the successful operation of the plant but which have not been shown because they would complicate the diagram and are not necessary for an understanding of the principles involved. A typical week's operation of this plant showed the following:

Refuse sand treated, 1,177,700 lb. (100 per cent.)

Good sand recovered, 1,005,800 lb. (85.4 per cent.)

Table 3 gives the mechanical and Table 4 the chemical analysis of the good sand recovered. It will be noted that the undesirable elements are concentrated in the finer materials, which are largely removed by the classifier, leaving only the small percentages shown in the good sand.

Operation of this plant for several years has proved that refuse sand can be reclaimed at a fraction of the cost of new sand. Furthermore, castings poured into molds made of reclaimed sand mixtures are equal in every respect to those poured into molds made of sand mixtures containing all or part new sand. In fact, sand reclaimed in this manne is much more uniform in quality than any ordinary grade of new molding sand. This uniformity, together with the fact that it is free from moisture, makes it an ideal sand for use in the production shop where close control of the sand quality is imperative.

TABLE 3.—*Mechanical Analysis of Reclaimed Sand*

SIEVE NUMBER	PER CENT. RETAINED	CUMULATIVE
8	None	None
12	0.27	0.27
14	0.91	1.18
20	1.60	2.78
28	10.65	13.43
40	51.82	65.25
48	26.61	91.86
70	6.66	98.52
100	0.79	99.31
140	0.24	99.55
200	0.06	99.61
−200	0.10	99.71

TABLE 4.—*Chemical Analysis of Fractions of Reclaimed Sand Retained on Screens*

	48 Mesh, Per Cent.	70 Mesh, Per Cent.	100 Mesh, Per Cent.	140 Mesh, Per Cent.	200 Mesh, Per Cent.	−200 Mesh, Per Cent.
Water..................	0.40	0.38	0.60	0.74	1.04	1.81
Carbon................	0.66	0.90	1.50	1.74	2.70	4.00
SiO_2....................	97.46	95.38	91.60	90.74	86.46	80.14
Al_2O_3..................	1.18	2.47	3.43	4.12	6.85	10.29
Fe_2O_3..................	0.10	0.06	0.69	0.61	0.74	0.71
FeO...................	0.36	0.52	1.48	2.05	2.33	3.12
CaO...................	Trace	Trace	Trace	Trace	Trace	Trace
MgO...................	Trace	Trace	Trace	Trace	Trace	Trace
K_2O...................			Not determined			
Na_2O..................			Not determined			
Total................	99.96	99.71	99.30	100.00	100.12	100.07

CONCLUSION

The author realizes that many of the points brought out in this paper could well have been amplified, but it was thought best to avoid lengthy discussions and give only those data pertinent to the questions involved.

The foregoing investigations were conducted at the plant of the Buckeye Steel Castings Co. and the writer wishes to acknowledge his indebtedness to that company for its kind permission to publish the results.

DISCUSSION

R. F. HARRINGTON, Boston, Mass.—The author has certainly contributed a great deal to our knowledge of molding sands.

He has referred to the necessity of removing the fines. I presume he refers to the difficulty that is encountered through their presence in the sand and their effect in creating a low fusing point. I wonder if there is any difficulty due to the low permeability of the sand which is created by these fines. If this is a factor, I should like to ask the author whether he has used bentonite, which forms conglomerate grains and in gray-iron molding-sand practice has made it unnecessary for us to remove these fines.

A. H. DIERKER.—Regarding the relative effect of fines on fusion and permeability, as I mentioned in the paper, the undesirable materials seem to congregate in the finer meshes. For that reason, from a fusion standpoint it is well to take out the fine material. The exact effect of fines on permeability, of course, is rather a problem. It would vary with the conditions under which the sand is used. But undoubtedly the fine material will decrease the permeability until it gets to a point where it cannot be used any more, and for that reason it is desirable to remove these fines.

I am not familiar with any practical use of bentonite in the steel foundry, although I know it is used to a considerable extent. In the iron foundry, of course, the temperatures are such that the fusion point of the sand is not so important as it is in the steel foundry, and for that reason a great deal of material can be left in the sand which it is not possible to leave in foundry sand. In other words, if the fine material is combined into larger grains, about the same size, the permeability has been maintained to the proper point and the fusion point is probably all right for iron, but it would not work, I think, for steel. I believe that if you accumulate the undesirable materials in that way into larger grains, you improve the permeability but lower the fusion point to a place where it would not be possible to make good castings in steel.

R. F. HARRINGTON.—Has it actually been proved that the use of bentonite might not take care of the situation even in steel, or is that a theory on your part?

A. H. DIERKER.—It is theory. I do not think the matter has ever been investigated.

S. W. UTLEY, Detroit, Mich. (written discussion).—Mr. Dierker's paper is exceedingly interesting and very timely, as this subject is receiving consideration by many of the steel foundries. His careful investigation of what takes place when silica sand and hot steel come in contact furnishes certain facts and describes certain principles of great value to all those studying this subject.

Steel foundrymen have observed almost since the beginning of the industry that when a casting was shaken out, the sand next to it and next to the gates, risers, and even nails projecting from it, had become blackened. Mr. Dierker describes this blackened condition as being caused by the formation of ferrous oxides, which, if the sand is used over and over again, without their removal, will gradually cause a decrease in its refractoriness. His study also indicates that outside of the sand that is close to the surface of the casting itself, which it is undesirable to use a second time, because of the presence around it of ferrous oxides, the heat has little effect on the sand grains themselves, and does not cause them to become appreciably more likely to be powdered by subsequent milling operations than the grains of new sand. He concludes that it is possible to reclaim silica sand for steel-foundry use, and describes in principle the method employed by the Buckeye Steel Casting Co. in doing this work, the principles involved being the crushing from the grains of the undesirable particles and the separation of them from the sand by means of a current of air.

Some other foundries are attacking the problem by the use of vibrating screens, and apparently are securing successful results. These are largely foundries making relatively small castings, on which the amount of silicate of iron produced by the fluxing action of the ferrous oxides adheres to the sand so closely that it is taken out as lumps of sand by the screening process. This is helped by the fact that many steel castings carry away with them to the cleaning room a considerable portion of the sand that is in contact with the surfaces, thereby eliminating from the heats a considerable portion of the undesirable silicates as well as those sand grains which have been cracked through contact with the hot metal. It is claimed for the screening method that it does not remove all the bonding material from the sand, as is the case when the separation is made by air under pressure, and that while the percentage of recovery may not be quite so high as by the other method, the saving in binder helps to offset this loss in reclaimed sand. The cost of the equipment is considerably less than that for the other method.

Mr. Dierker's work might well be extended to an investigation of dry sand molds. A better knowledge of the absorption of heat by the mold might lead us to some valuable conclusions in respect to the gating of large castings, and give other data of value to the steel foundryman.

Influence of Rate of Cooling on Dendritic Structure and Microstructure of Some Hypoeutectoid Steel

By Albert Sauveur,* Cambridge, Mass., and C. H. Chou†

THE following experiments were conducted in order to study the influence of the rate of cooling through and below solidification on the dendritic structure (macrostructure) and microstructure of some hypoeutectoid steel. The steel selected was of commercial grade and had the following composition: C, 0.40 per cent.; Mn, 0.85; Si, 0.70; P, 0.099; S, 0.043. After melting in vacuum in an Arsem furnace, the various samples were allowed to solidify and to cool to room temperature as indicated in Fig. 1. Samples were thus obtained representing all possible combinations of slow and fast cooling through the various ranges of temperatures indicated, namely: (1) zone of solidification or primary crystallization, (2) zone of granulation, and (3) zone of secondary crystallization. The location of the different temperature zones in the iron-carbon equilibrium diagram is shown in Fig. 2. The authors adopted Belaiew's notations. The designations of the various samples readily indicate their treatment, as will be apparent from Table 1.

TABLE 1.—*Rate of Cooling of Samples*

Designation of Sample	Zone of Solidification	Zone of Granulation	Zone of Secondary Crystallization
SSS	slow	slow	slow
SSF	slow	slow	fast
SFS	slow	fast	slow
SFF	slow	fast	fast
FSS	fast	slow	slow
FSF	fast	slow	fast
FFS	fast	fast	slow
FFF	fast	fast	fast

Sample SSS.—This sample was slowly solidified and cooled to room temperature in the crucible in which it was melted. The dendritic (macro) structure is shown in Fig. 3. The dendrites are sharp and dis-

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* Gordon McKay Professor of Metallurgy and Metallography, Harvard University.
† Formerly with the National Tube Co., Lorain, Ohio. Now in China.

tinct. The microstructure (Fig. 4) is of the Widmanstäten type with coarse ferrite bands in places.
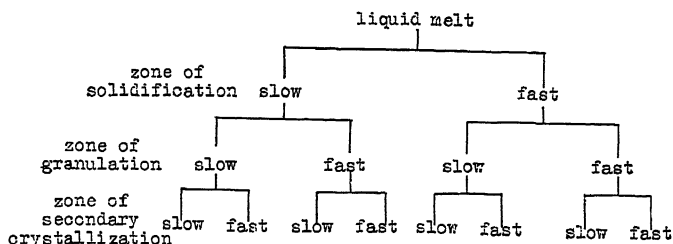
FIG. 1.—SAMPLES COOLED AT ROOM TEMPERATURE.

Sample SSF.—This sample was allowed to cool slowly in the furnace until a temperature of some 900° C. had been reached, when the crucible
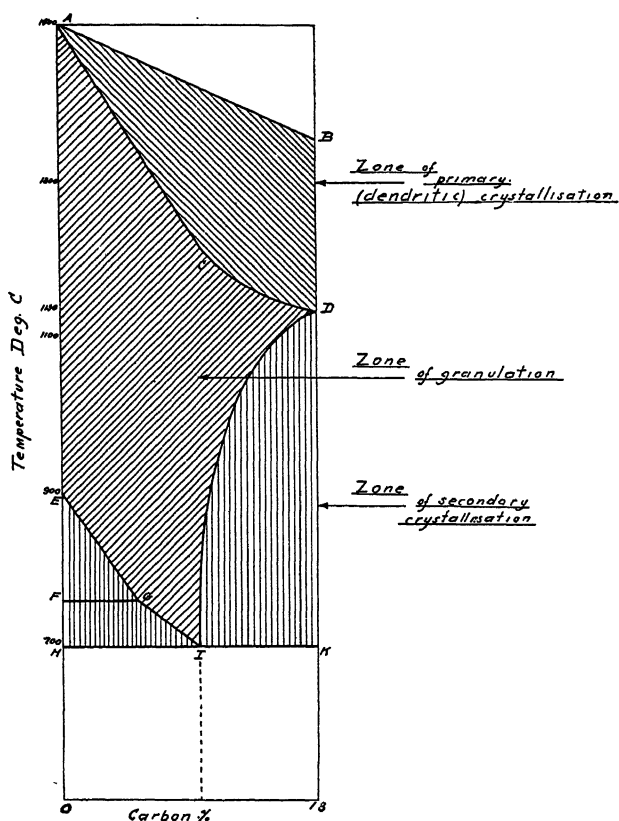
FIG. 2.—TEMPERATURE ZONES IN IRON-CARBON EQUILIBRIUM DIAGRAM.

and its contents were removed from the furnace and cooled in air to room temperature. The dendritic structure (Fig. 5) is not unlike that of the
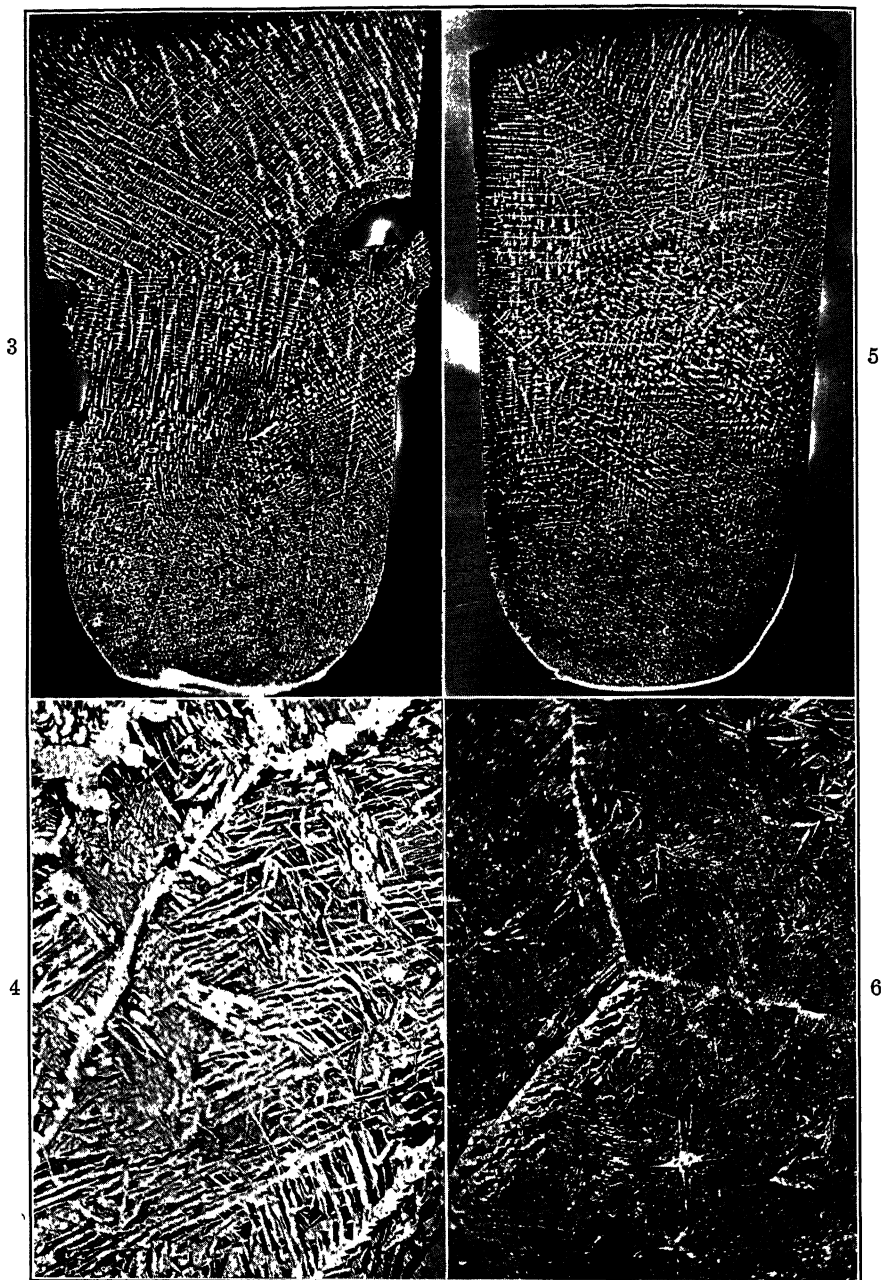
FIG. 3.—DENDRITIC STRUCTURE, SAMPLE SSS. × 3.
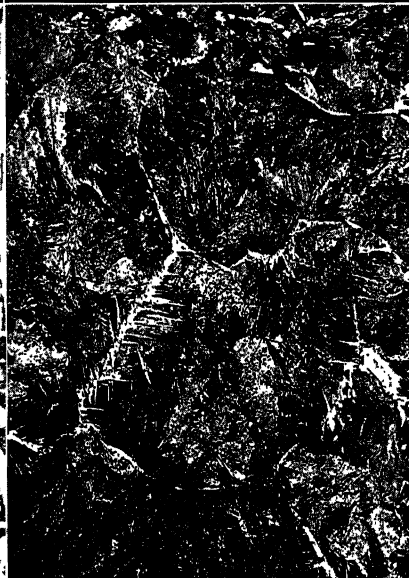FIG. 4.—MICROSTRUCTURE, SAMPLE SSS. × 100.
FIG. 5.—DENDRITIC STRUCTURE, SAMPLE SSF. × 3.
FIG. 6.—MICROSTRUCTURE, SAMPLE SSF. × 100.
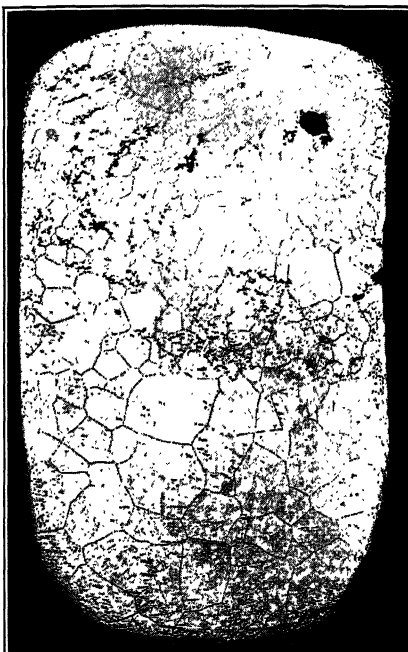All samples commercial steel.
Reduced ⅕; original magnification given.
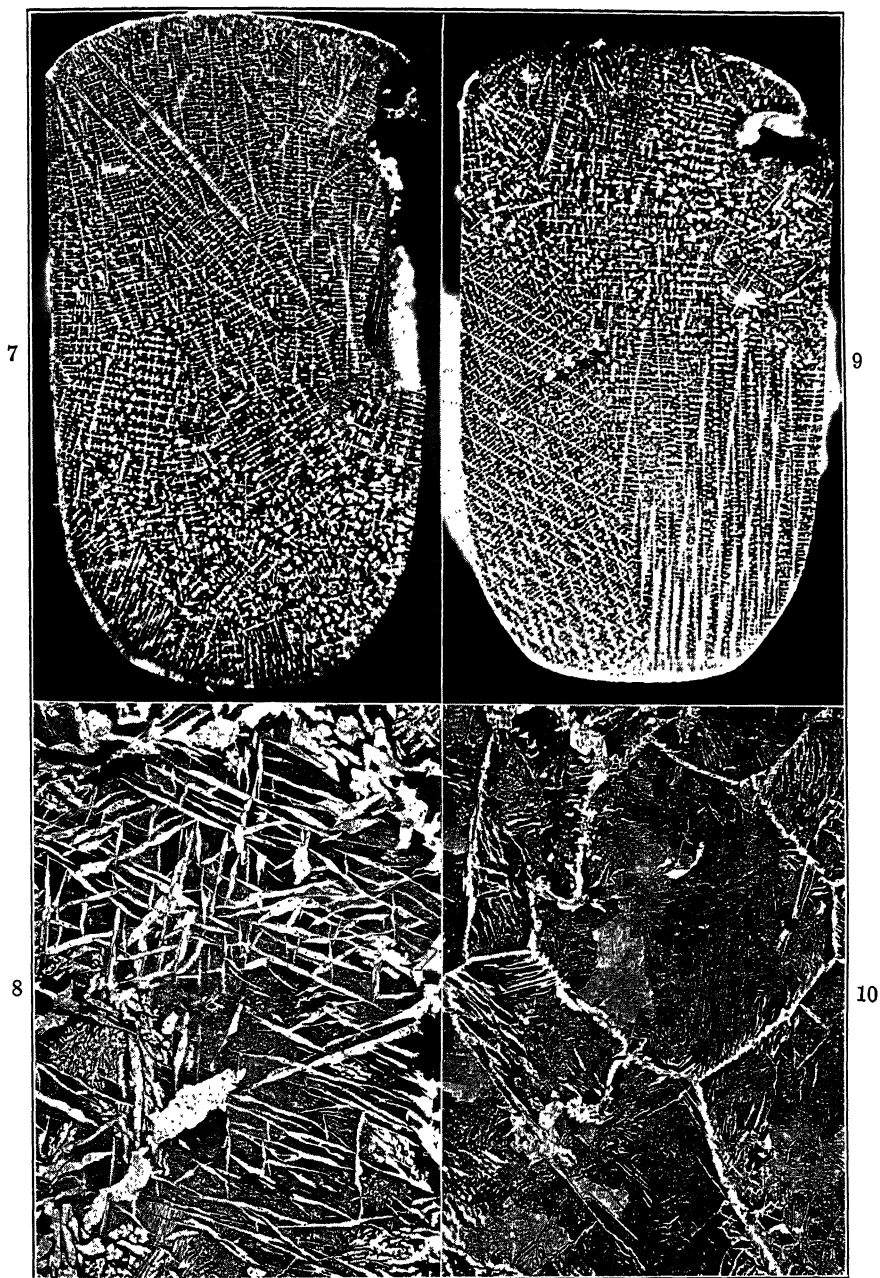
FIG. 7.—DENDRITIC STRUCTURE, SAMPLE SFS. × 3.
FIG. 8.—MICROSTRUCTURE, SAMPLE SFS. × 100.
FIG. 9.—DENDRITIC STRUCTURE, SAMPLE SFF. × 3.
FIG. 10.—MICROSTRUCTURE, SAMPLE SFF. × 100.
All samples commercial steel.
Reduced ⅕; original magnification given.

previous sample but the microstructure (Fig. 6) is decidedly of the network pattern. The meshes are sorbitic rather than pearlitic.

Sample SFS.—After the melt in the furnace had reached a temperature of about 1300° C. it was removed and cooled in air to a temperature of about 850°, when it was placed in a furnace previously heated to 850° and cooled slowly with the furnace to room temperature. The dendritic structure is shown in Fig. 7 and the microstructure in Fig. 8. The latter is of the Widmanstätten type.

Sample SFF.—The melt was removed from the furnace after it had reached a temperature of some 1300° C. and cooled in air to room temperature. A very clear dendritic structure was obtained (Fig. 9), and a distinct network microstructure (Fig. 10).

Sample FSS.—After the steel had been melted it was taken out of the furnace and cooled in air to a temperature of some 1300° to 1350° C., when it was placed in another furnace which had been preheated to a temperature of 1000° C. and allowed to cool to room temperature in that furnace. The macrostructure (Fig. 11) is finely dendritic and the microstructure (Fig. 12) of a mixed type, neither clearly of a network pattern nor Widmanstätten.

Sample FSF.—This sample was removed from the furnace when still liquid and cooled in air to a temperature of some 1300° to 1350° C., placed in another furnace, preheated to 1000° C., cooled in that furnace to 850° C. when it was taken out and the cooling completed in air. The macrostructure (Fig. 13) is finely dendritic, while the microstructure (Fig. 14) exhibits a coarse ferrite network.

Sample FFS.—The melt was removed from the furnace, solidified and cooled in air to a temperature of about 850° C. when it was placed in another furnace preheated to 800° C. and allowed to cool to room temperature. The macrostructure (Fig. 15) is finely dendritic and the microstructure (Fig. 16) of a mixed type.

Sample FFF.—This sample was removed from the furnace when still liquid and allowed to cool in air. The macrostructure (Fig. 17) is finely dendritic and the microstructure (Fig. 18) of a network pattern with thick ferrite boundaries.

Sample SSS_1.—In order to obtain slower rates of cooling, a melt of the same steel to be designated hereafter as SSS_1 was solidified and cooled in the furnace in which it was melted at the rate of 1° C. per minute through suitable regulation of the current. The resulting microstructure (Fig. 19) is distinctly Widmanstätten and should be compared with the microstructure of SSS (Fig. 4), less slowly cooled. The macrostructure, however, is now but confusedly dendritic (Fig. 20). It seems reasonable to assume that this absence of marked dendritic segregation is due to the diffusion of the impurities made possible by very slow cooling. On
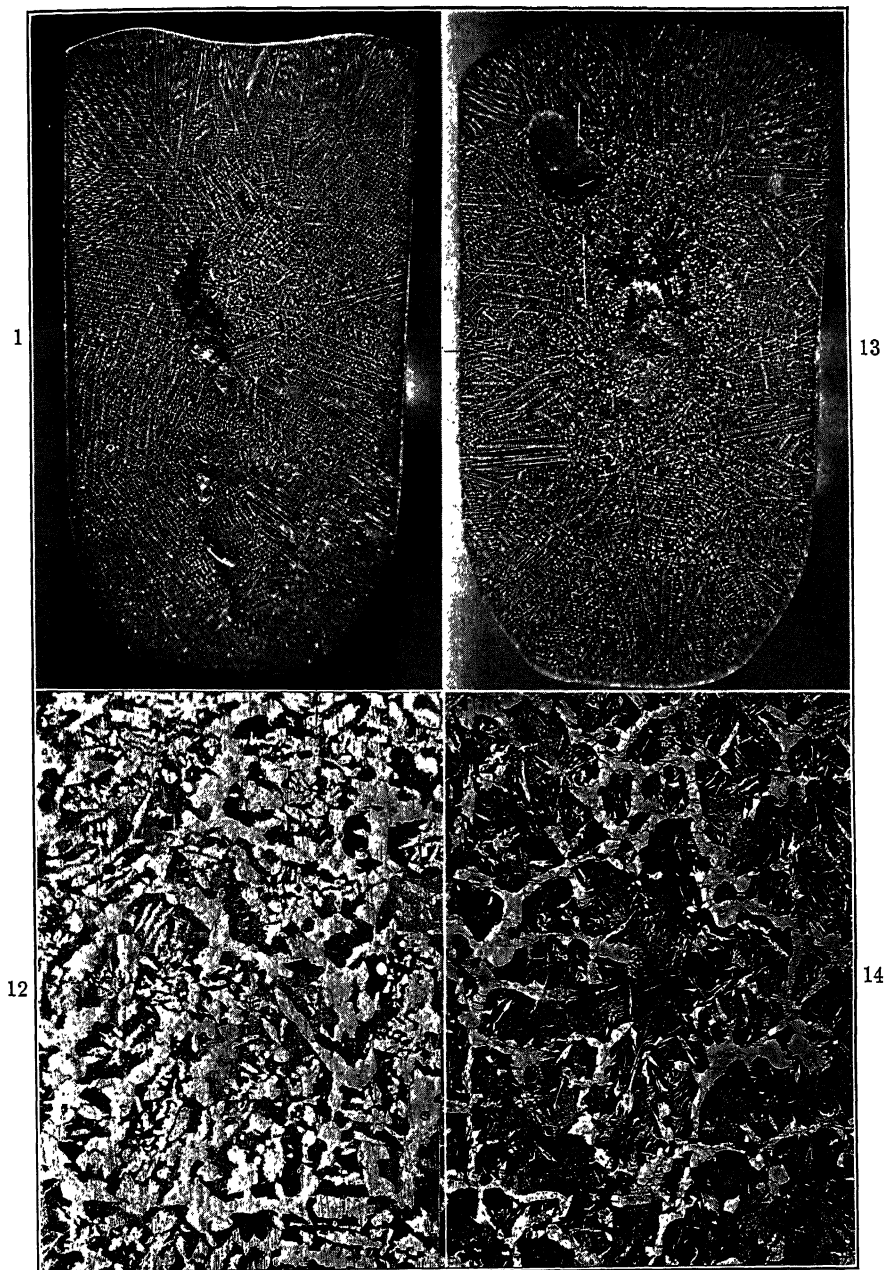
FIG. 11.—DENDRITIC STRUCTURE, SAMPLE FSS. × 3.
FIG. 12.—MICROSTRUCTURE, SAMPLE FSS. × 100.
FIG. 13.—DENDRITIC STRUCTURE, SAMPLE FSF. × 3.
FIG. 14.—MICROSTRUCTURE, SAMPLE FSF. × 100.
All samples commercial steel.
Reduced ⅕; original magnification given.
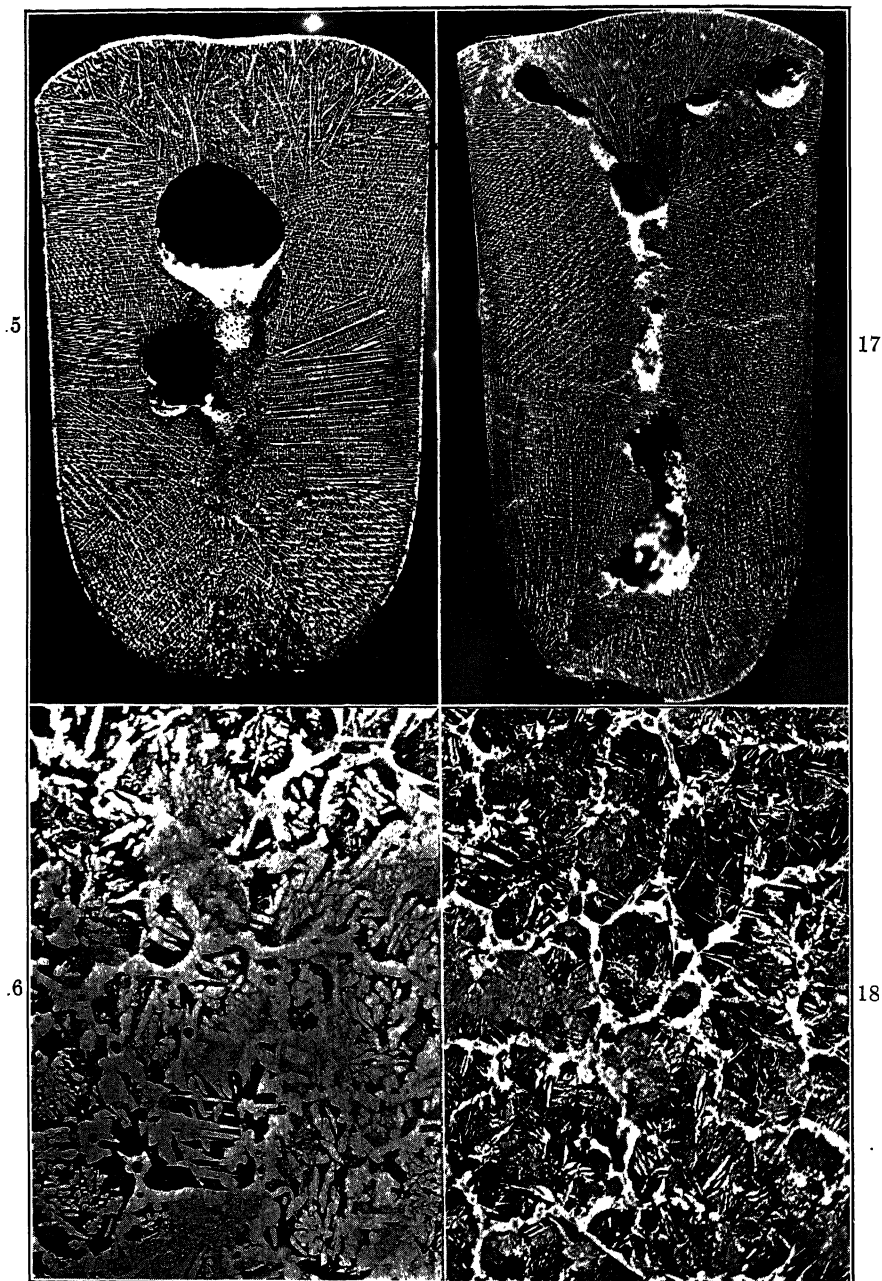
FIG. 15.—DENDRITIC STRUCTURE, SAMPLE FFS. × 3.
FIG. 16.—MICROSTRUCTURE, SAMPLE FFS. × 100.
FIG. 17.—DENDRITIC STRUCTURE, SAMPLE FFF. × 3.
FIG. 18.—MICROSTRUCTURE, SAMPLE FFF. × 100.
All samples commercial steel.
Reduced ⅕; original magnification given.

the other hand, the slowly solidi-
fied samples of our first series
of experiments have larger den-
drites than the more rapidly
cooled ones.

INFLUENCE OF IMPURITIES

In order to ascertain to what
extent the impurities found in
commercial steel affect the
macrostructure and microstruc-
ture of cast ingots, these experi-
ments were repeated with a steel
of great purity, except for its sili-
con content. It had the follow-
ing composition: C, 0.53; Mn,
0.058; Si, 0.205; P, 0.006; S,
0.034 per cent. It was sub-
stantially free from manganese.
Let it be recalled that the com-
mercial steel contained 0.85 per
cent. manganese and 0.099 per
cent. phosphorus. To avoid the
reproduction of an excessive
number of photomicrographs
only the SSS and FFF samples
of this series are shown (Figs. 21
to 24). The dendritic structure
was fine and indistinct in all
samples — after slow cooling
through the thermal critical
range the microstructure was
more distinctly Widmanstätten
than the structure of the corre-
sponding samples of the com-
mercial steel—all samples cooled
through their critical range had a
network structure.

It is generally possible to
bring out clearly the macro-
grains resulting from the granu-
lation of the dendrites in cooling
through the granulation range
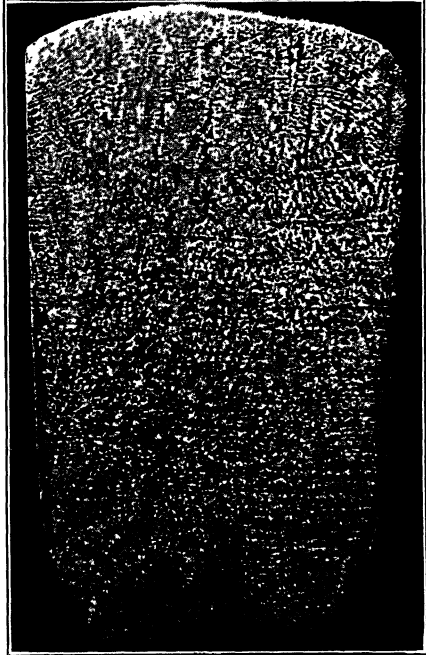
FIG. 19.—MICROSTRUCTURE, SAMPLE SSS₁.
× 100.

FIG. 20.—DENDRITIC STRUCTURE (CON-
FUSED), SAMPLE SSS₁.   × 3.

Both samples commercial steel.
Reduced ⅙; original magnification given.
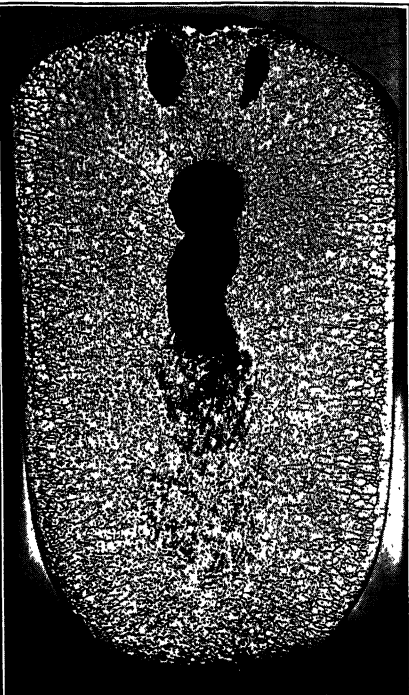
FIG. 21.—DENDRITIC STRUCTURE, SAMPLE SSS.   × 3.
FIG. 22.—MICROSTRUCTURE, SAMPLE SSS.   × 100.
FIG. 23.—DENDRITIC STRUCTURE, SAMPLE FFF.   × 3.
FIG. 24.—MICROSTRUCTURE, SAMPLE FFF.   × 100.
All samples nearly pure steel.
Reduced ⅕; original magnification given.

FIG. 25.—MACROGRAINS, SAMPLE SSS. × 3.
FIG. 26.—DENDRITIC STRUCTURE, SAMPLE SSS. × 3.
FIG. 27.—MACROGRAINS, SAMPLE SFS. × 3.
FIG. 28.—DENDRITIC STRUCTURE, SAMPLE SFS. × 3.
All samples nearly pure steel.
Reduced ¼; original magnifications given
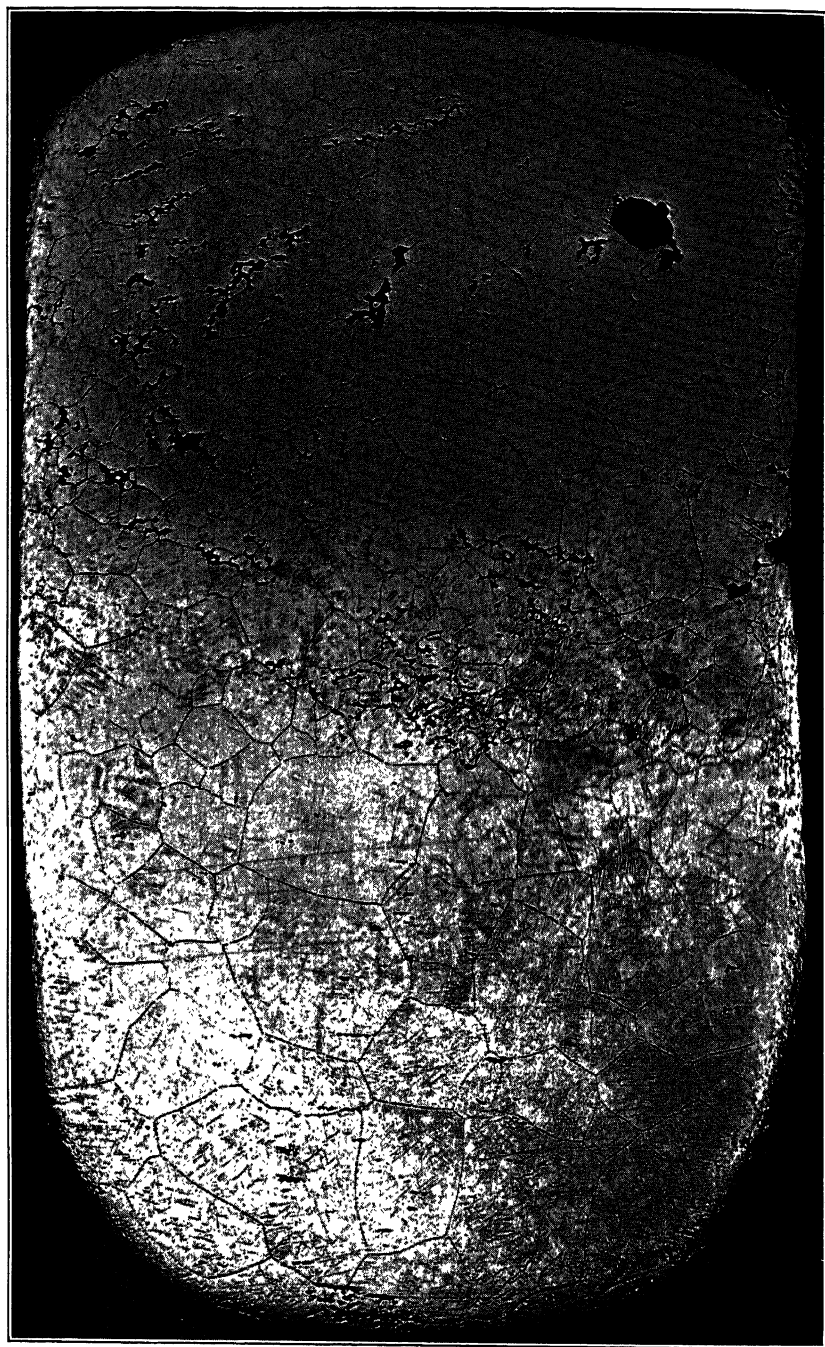
FIG. 29.—SAME AS FIG. 25. × 6.
Sample nearly pure steel.
Reduced ⅕; original magnification given.
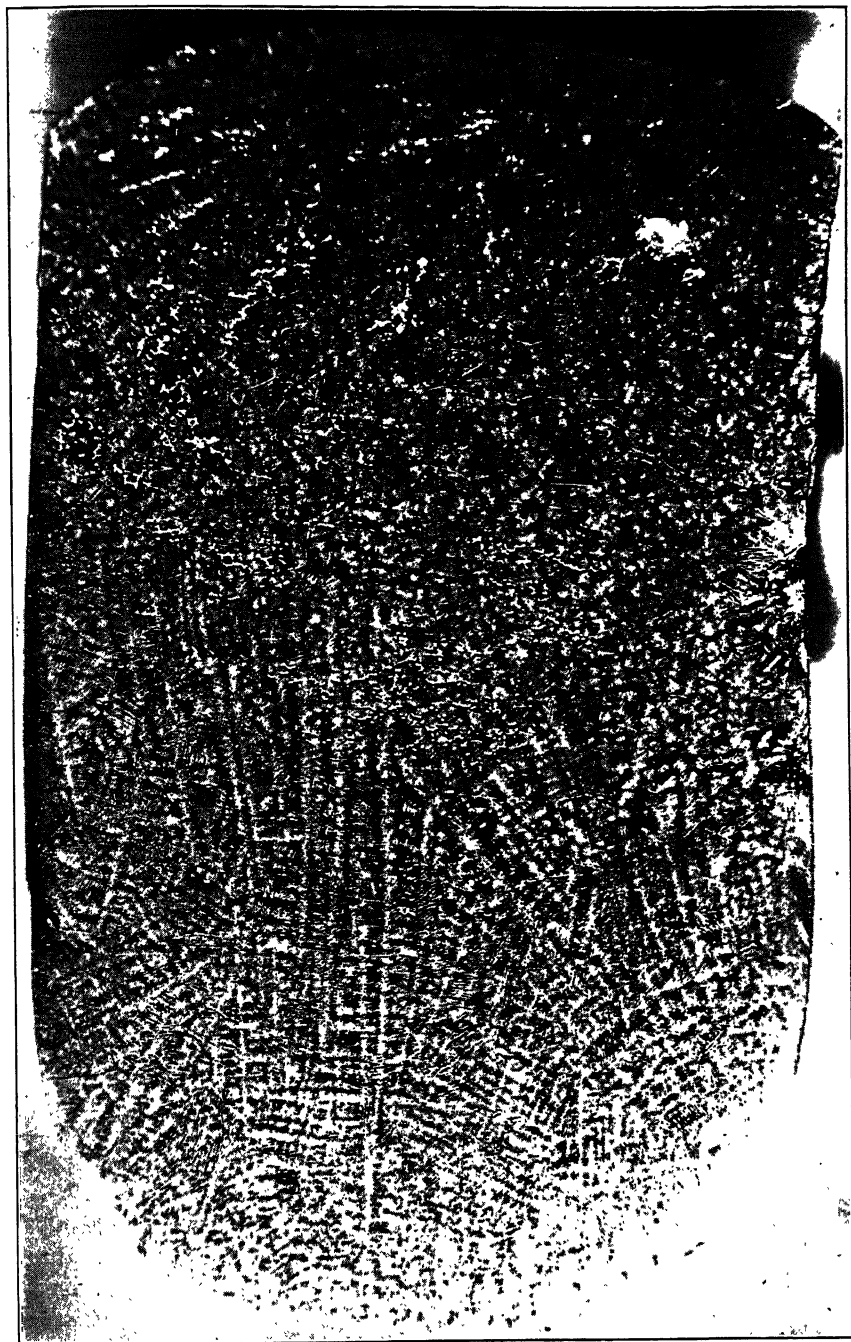
FIG. 30.—SAME AS FIG. 26. × 6.
Sample nearly pure steel.
Reduced ⅓; original magnification given.

by etching deeply with 10 per cent. nital, followed by polishing until only the grain boundaries remain. It is believed that they indicate the size of the austenite grains, as they exist immediately before their breaking up into a ferrite-cementite aggregate. It will suffice to reproduce here a few of the many structures obtained. Figs. 25 and 26 show, respectively, the macrograins and the dendritic structure of the pure steel sample SSS, and Figs. 27 and 28 similar structures of the pure
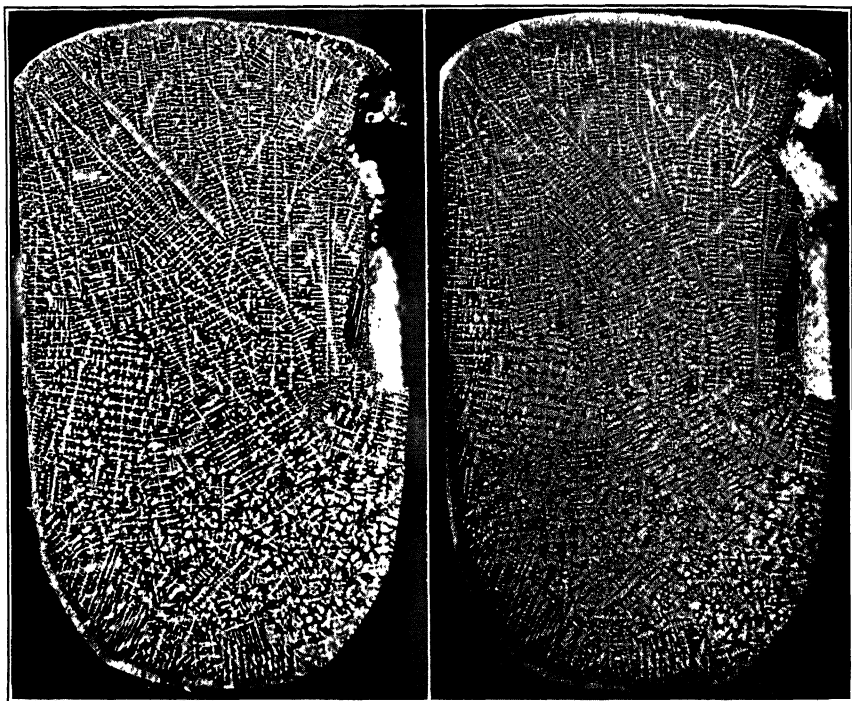
FIG. 31.—DENDRITIC STRUCTURE, SAMPLE SFS COMMERCIAL STEEL, AS CAST. × 3.

FIG. 32.—SAME AS FIG. 31 AFTER HEATING 1 HR. AT 1000° C. AND COOLING SLOWLY. × 3.

Reduced ⅕; original magnifications given.

steel sample SFS. These structures are magnified 3 diameters. The treatments applied differ only in the rate of cooling through the granulation range, which was slow in sample SSS and fast in sample SFS. The macrograins in sample SFS are much smaller. The structures of sample SSS have been enlarged to 6 diameters in Figs. 29 and 30.

It is well known that dendritic segregation is not erased by heating to high temperatures followed by slow cooling. This is well illustrated in Figs. 31 and 32 of sample SFS commercial, respectively, as cast and after heating for 1 hr. at 1000° C. followed by slow cooling.

CONCLUSIONS

From the results reported in this paper and from those of many other experiments, the following conclusions appeared justified.

While these conclusions refer only to the two steels investigated, it is believed that they would be found applicable to carbon steels in general.

1. *Dendritic Structure vs. Purity.*—The dendrites of the commercial steel are considerably larger and more clearly defined than those of the pure steel.

2. *Macrograins vs. Purity.*—For like treatment the macrograins of the commercial steel are smaller than those of the pure steel.

3. *Microstructure vs. Purity.*—For like treatment the Widmanstätten structure after slow cooling through the thermal critical range is much more pronounced in the pure steel.

4. *Dendritic Structure vs. Speed of Solidification.*—The dendrites of the four samples of commercial steel slowly solidified are substantially larger than those of the four samples more rapidly solidified. In the pure steel, there is no appreciable difference between the dendritic pattern of the samples slowly and rapidly solidified.

5. *Size of Macrograins vs. Rate of Cooling through the Granulation Range.*—The slower the cooling through the granulation range, the larger the macrograins.

6. *Microstructure vs. Size of Macrograins.*—The larger the macrograins, the more marked the Widmanstätten type of structure after slow cooling through the thermal critical range.

7. *Microstructure vs. Size of Dendrites.*—The less pronounced the dendritic structure, the more pronounced the Widmanstätten structure after slow cooling through the thermal critical range.

8. *Microstructure vs. Rate of Cooling through the Thermal Critical Range.*—Slow cooling through the thermal critical range induces the formation of a Widmanstätten structure; rapid cooling induces the formation of a network structure.

DISCUSSION

R. G. KENNEDY, JR., Washington, D. C.—Several years ago, at the Pennsylvania State College, under the direction of Professor Knight, we did some work on the relation of the dendritic structure to the size of the micrograins for the same rates of cooling through the granulation zone; *i. e.*, from the solidification temperature down to around 900° C. We used ordinary samples. We found that, for identical cooling rates through this range, the larger dendrites gave larger micrograins.

Comparing Fig. 5 with Fig. 13, it can be seen that the dendrites in Fig. 5 are coarser, while the conditions of cooling below the solidification zone for those two samples are the same; also, the size of the micrograins is appreciably different. The dendrites of Fig. 5 are not much larger, but are coarser, and correspondingly, micrograins of Fig. 5 are larger than those of Fig. 14.

B. STOUGHTON, Bethlehem, Pa.—This research is exceedingly interesting in connection with steel castings. It confirms the prophecies, if I may call them prophecies, or at least the deductions, that Professor Sauveur has been making for years. It shows in a striking way how the different zones produce different structures in steel. I hope that Professor Sauveur, or someone, will correlate these with some tensile strengths and ductility tests indicating the effect of the different structures on the steels, because from the steel-casting standpoint that certainly is very important. For instance, is a sorbitic steel with large micrograins worse in tensile strength or in ductility, or both, than steel with Widmanstätten structure with small grains?

Professor Sauveur has shown us how to control these structures to a certain extent and it is very important to know what to do when castings do not exactly come up to specifications.

I do not know how many have seen the micrograin structure of the 1.60 manganese steel that is used so much for rail and for structural work, such, for example, as the Kill Van Kull bridge. If a metallurgist were to have a terrible nightmare, it would not be any worse than the micrograin structure he would see in looking at the Kill Van Kull bridge. There are great coarse grains with a sort of sorbitic structure and an entire absence of Widmanstätten structure. But apparently the Port of New York Authority went into the problems of that steel very carefully before they permitted the change from nickel steel to this low-manganese steel, and apparently it has proved that that steel is all right. It would be very interesting if we had some way of knowing the influence of different types of structure on the properties, for future reference.

On page 107 Professor Sauveur has what he calls a pure steel. I will grant it is a pure steel with the exception of 0.205 silicon. I wonder if that is a misprint. In view of the effect of silicon on the grain structure, it seems to me that this is not exactly a pure steel from the standpoint of analysis.

H. G. KESHIAN, Waterbury, Conn.—The point brought out by Professor Stoughton is very important; because, after all, it is the physical properties of steel that we are essentially interested in. Notwithstanding the intimate relation that exists between the structure of metals and their physical properties, we are not always able to establish definitely that relation for all types of structures. This is particularly true with macrostructures.

Professor Sauveur stated that when dendritic structure is present in steel in pronounced degree it causes weakness. Whether this statement applies to cast steel or forged product, I believe it requires some modification. It is true that in numerous instances it has been shown that excessively dendritic structure results in lower mechanical properties than steel not so dendritic; but by no means is this invariably so. On the other hand, there are many other instances where an intensely dendritic steel, whether cast or forged, has exhibited equally good physical properties; in some other cases, even better than nondendritic steel. When we consider the forged and heat-treated dendritic steels, both physical and service tests have shown even more clearly that the presence of this type of structure is not always an indication of weakness.

The authors do not state the rate of cooling of their test specimens in terms of so many degrees per unit of time. The rate of cooling of the molten metal in the mold is one of the most important factors in the development of dendritic structure; therefore, when comparing the relative intensity of dendritic structure of various steels the rate of cooling in each case should be known definitely, particularly where the size of ingot is as small as the authors have used. A more accurate rate of cooling than the one adopted by the authors might not have materially affected the results of their experiments; nevertheless, it seems to me that a constant rate of cooling for the specimens compared, if expressed in numerical terms, would have made the authors' work doubly valuable.

The authors found that the dendritic structure could be more clearly revealed by etching in commercial steel than in what they consider pure steel. It is to be noted that the essential difference in the chemical composition of the two steels was in their phosphorus and manganese contents. Commercial steel contained both of these elements in much larger amounts. Now, the revealing of dendritic structure will depend on the degree of dendritic condition present in the steel; also on the etching characteristic of the metal. With the same type of steel, a large number of experiments on macroetching by the writer showed that the addition of manganese materially increases the attack of acid on steel, so that the resulting structure becomes more contrastive under the same conditions of etching. It was found, for instance, that steel containing 0.19 per cent. carbon and 0.74 manganese after acid etching lost 0.705 gram per square centimeter. Another steel containing 0.37 per cent. carbon and 1.36 per cent. manganese lost 1.06 g. with the same period of etching. In the second case, the metal was etched too deeply and presented more relief effect than in the first case. If both steels had the same degree of dendritic condition before etching, it is to be expected that the dendritic pattern would be brought out more clearly in the second steel than in the first steel. The tendency of manganese to increase the attack of acid on steel seems to be true on other types of steel containing appreciable amounts of manganese. For instance, the Tentative Recommended Practice for Macroetching by the American Society for Steel Treating calls for 45 min. etching for S.A.E. No. 1050 steel, but 30 min. for S.A.E. No. 1350 steel, the average content of manganese being 0.65 and 1.05 per cent. respectively. If the authors used the same period of etching, it is very likely that their specimens containing manganese may be overetched and reveal the dendrites in a greater relief. These statements, however, are not offered to explain the more dendritic character of their commercial steel, but to show the effect of the time of etching on the development of dendrites.

The first conclusion of the authors, that "the dendrites of the commercial steel are considerably larger and more clearly defined than those of the pure steel," is worthy of serious consideration and, if it is to be interpreted correctly, the presence of larger and more clearly defined dendrites should indicate greater impurity in the steel. Then it is up to the steel mills to reduce the dendritic condition in their product by reducing the amount of impurity in the metal. Yet the problem of dendritic steel does not seem to be as simple as it appears. We get greater dendritic condition with more carbon. Shall we, then, consider carbon an impurity? If the presence of impurity causes weakness by promoting excessive dendritic structure, why is it that high carbon steel is not weaker than low-carbon steel? Some of the chromium-nickel steels of the S.A.E. series are prone to be dendritic; much more so than plain carbon steels. Shall we consider these steels very impure and weak? On the contrary, they represent some of the strongest steels, which have made present-day high-speed machinery possible. This paradox, or dilemma, whatever we might call it, evidently is due to a lack of proper definition of what constitutes an impurity and what does not.

A. Sauveur (written discussion).—I fully agree with Professor Stoughton in regard to the importance of finding the relation between the physical properties and the different types of dendritic and microstructures described in our paper. We have some information on the subject, but it is not nearly so complete as it should be. The importance of dendritic segregation in castings is obvious, if we bear in mind that once produced it cannot be erased by any of the usual annealing treatments to which castings are subjected. If it is admitted that a coarse dendritic structure is objectionable, we should attempt to prevent its formation by suitable regulation of the rate of solidification, the casting temperature and composition. There is no doubt in our minds that the purer the steel, the less the dendritic segregation. We are inclined to

believe that a pronounced Widmanstätten structure is more prone to produce weakness than a large network structure of sorbitic grains, which would explain the satisfactory condition of the 1.60 per cent. manganese steel to which Professor Stoughton refers. Assuming this to be true, it would point to the advisability of removing steel from the annealing furnace while still slightly above the critical temperature followed by air cooling. It could then be reheated to a temperature substantially below the critical range and cooled slowly in order to remove residual strains.

In regard to the percentage of silicon present in what we have termed pure steel, namely 0.205 per cent., it is not a misprint. On that ground Professor Stoughton may be right in his objection to describing it as pure steel. We had more in mind the nearly complete absence of manganese and phosphorus by which they are sharply differentiated from commercial steels.

Replying to Mr. Keshian's remarks, we did not mean to take the position that any steel exhibiting a marked dendritic structure was necessarily weak or of inferior quality. Many other factors contribute to the physical properties of steel. A coarse dendritic structure we believe to be a source of weakness, but it does not follow that of two steels the one exhibiting the more pronounced dendritic segregation is of necessity inferior in mechanical properties. That would be true only if the two steels were exactly of the same composition, and had been subject to identical mechanical and thermal treatments.

In regard to the rates of cooling of our ingots, it is not possible to state them in degrees per unit of time. We have explained in our paper what we meant in every instance by fast and slow cooling. We do not deny the accuracy of Mr. Keshian's contention that the presence of manganese accelerates dendritic etching, but we do not see what bearing this observation has on the results reported by us. Each sample was subjected to the action of the reagent until its macrostructure was revealed.

Mr. Keshian asks why high-carbon steels, being more dendritic than low-carbon steels, are not weaker? Judging from the results of our experiences, the intensity of dendritic segregation does not increase with the carbon content. It seems to reach a maximum at some 0.40 to 0.50 per cent. carbon. With that composition, at least, the dendrites are larger and more clearly defined. Admitting, however, that carbon intensifies dendritic segregation and, therefore, promotes mechanical weakness, it also produces pearlite, which greatly increases the strength. A high-carbon steel, even if more intensely dendritic, obviously may have mechanical properties greatly superior to those of a low-carbon, less dendritic steel—and so it is with the chromium-nickel steels mentioned by Mr. Keshian.

Transformation of Austenite at Constant Subcritical Temperatures

By E. S. Davenport* and E. C. Bain,† Kearny, N. J.

When annealed carbon, or low-alloy, steels are suitably heated the ferrite (alpha iron solid solution) and the carbide, of which they are composed, react together to form a single solid solution of carbon (and other elements) in gamma iron (austenite). This reaction may begin only at a certain minimum temperature called the eutectoid temperature. The first ferrite and carbide thus to react together do so in definite proportions known as the eutectoid composition. With further heating the original constituent that is present in excess is dissolved in the austenite until exhausted. Whether the excess constituent be ferrite (hypoeutectoid steels) or carbide (hypereutectoid steels) the procedure is much the same, and upon slow cooling the homogeneous austenite expels the excess of either (proeutectoid ferrite or carbide) until the eutectoid composition is reached. Thus the reaction upon heating is strictly reversed upon cooling and accordingly an equilibrium diagram of this process may be constructed.

Such an equilibrium diagram concerns itself only with the temperatures involved and with the proportions and compositions of the phases developed under conditions that suffice to permit equilibrium. Specifically it has no concern for the type or mode of distribution of these constituents nor with any extra-equilibrium conditions such as undercooling, which is almost universally encountered in metals. Actually, however, of great importance is the sluggishness toward equilibration caused by the not inconsiderable time involved in diffusion. Thus instead of the theoretical transformation point A_E, we find for a certain rate of heating or cooling the use of the designations Ar and Ac (transformation temperature found on cooling and upon heating). These figures obviously have no particular meaning except as measured and expressed for a definite heating or cooling rate, and represent the *apparent* temperature displacement caused by an inadequate time allowance.

In this paper are presented the results of a study of the time required for the transformation of austenite to ferrite and carbide at a variety of temperatures and also of the time required for the reaction austenite→ martensite at the temperatures at which this reaction occurs instead of

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* United States Steel Corpn., Research Laboratory.
† Hunt Medallist, 1929.

the one first mentioned. In short, this study proposes the addition of the time factor to the iron-carbon diagram.

TIME REQUIRED FOR TRANSFORMATION OF AUSTENITE

Some ideas as to the time required for the transformation of austenite have been offered by earlier investigators. Portevin and Garvin,[1] Chapin[2] and Lewis[3] have observed the unexpectedly low rate of the reaction at temperatures in the vicinity of 300° C. (575° F.) for carbon steels, and DeLong and Palmer[4] have described the same type of sluggishness in high-speed steel at its analogous temperature range in the vicinity of 600° to 650° C. (1100° to 1200° F.). Many years ago one of the present writers observed the slow transformation of austenite in a low-alloy steel cooled quickly to about 225° C. (440° F.) in hot oil. The specimen was immediately transferred to a Rockwell hardness tester but its hardness could not be measured accurately on account of the continuous expansion accompanying the transformation, which caused the needle to traverse the dial at a moderately rapid rate for several minutes.

It is well known that rapid cooling will undercool austenite for several hundred degrees prior to its transformation. It is equally well known that the degree of rapidity of cooling has a profound effect upon the nature of the product of the transformation. For example, a slow cooling is said to produce coarse lamellar pearlite while rapid cooling may produce troostite or even martensite. The present authors have adopted the viewpoint that any restricted portion of a piece of steel acquires a given structure upon transformation as a result (almost wholly) of the temperature at which transformation occurred. Obviously the temperature of transformation of this infinitesimal of austenite may have been determined by the rate of cooling of the whole mass, but it owes its final structure to the circumstance of its having transformed at a certain subcritical temperature. The specimen as a whole transformed at a variety of temperatures, perhaps, but if so its structure also covered a range of characteristics. In most cases, the rate of cooling of a specimen of steel may be the means of determining the temperature at which a given portion of the metal inaugurates its transformation. That the rate of cooling *per se* has any effect upon the product or velocity of the transformation, except by this indirect means, seems extremely doubtful.

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[1] A. Portevin and M. Garvin: Fundamental Investigation of the Influence of the Rate of Cooling on the Hardening of Carbon Steels. *Jnl.* Iron and Steel Inst. (1919) **99**, 469.

[2] W. R. Chapin: Properties of Some Steels in the Hardening Range. *Trans.* Amer. Soc. Steel Treat. (1922) **2**, 507.

[3] D. Lewis: Transformation of Austenite into Martensite in an 0.8 per cent. Carbon Steel. *Jnl.* Iron and Steel Inst. (1929) **119**, 427.

[4] B. H. DeLong and F. R. Palmer: What Happens when High-speed Steel is Quenched. Trans. Amer. Soc. Steel Treat. (1928) **13**, 420.

That this viewpoint is wholly tenable seems established by the results of the authors' investigations, which were all obtained from comparatively small specimens that could be rapidly cooled as pure austenite to any desired temperature and then given no choice but to transform *at that constant temperature*. The temperatures for transformation that were studied cover the range from the lower critical down to room temperature. The general trend of the effect of transformation temperature upon the time of transformation and upon the nature of the product was worked out first in detail for a single steel. This necessitated study at a great number of temperatures, and to reduce the task to practicable dimensions other steels were studied less thoroughly and the intermediate temperature effects were interpolated on the basis of the more minutely observed behaviors encountered in the first representative steel. The need for this procedure will become evident in the following discussion.

METHODS OF INVESTIGATION

In order to observe the progress of austenite transformation at any definite temperature it is necessary, obviously, to cool the properly heated specimen rapidly to the temperature for study and then to maintain it at that temperature within narrow limits. The quenching to this subcritical temperature must be rapid enough to preserve the austenite essentially unchanged down to the observation temperature, and to prevent transformation from occurring at any temperature above (or below) the one chosen for study.

Specimens.—These restrictions demand the use of (1) thin specimens with high surface-to-mass ratio and (2) a quenching bath of high cooling power

FIG. 1.—TIME-TEMPERATURE QUENCHING CURVE.

automatically controlled at constant temperature. For all practical purposes these conditions were obtainable. Steel specimens about 0.060 in. thick were found to cool rapidly enough in a molten lead bath. They were sufficiently thick, on the other hand, to withstand Rockwell hardness measurements with inconsequential error. Therefore the various steels were obtained in the form of flat strip, usually about ½ in. wide. Such strip was suitable for microscopic examination and rigid enough for the dilatometric investigation described below.

Quenching Mediums.—Information from various sources led to the belief that molten metal baths would be best suited to this investigation.

For the lower temperatures the lead bath was alloyed with bismuth to form the eutectic composition, which remains molten down to about 135° C. (275° F.). To check the cooling rate of the flat specimens, some tests were made to discover the time-temperature behavior of the quenching. Thermocouples welded to specimens sufficed; other thermocouples of such dimension as to be thermally similar to the specimens were also quenched and their behavior observed. Fig. 1 illustrates the cooling rate of the lead quench at two representative temperatures. In the light of the subsequent investigations the quenching rate appears in general more than sufficient to prevent any part of the transformation from occurring at temperatures intermediate between heating temperature and constant bath temperature, the only exception being in the case of one or two steels in the vicinity of 570° C. (1000° F.). It may be assumed that the specimens transformed only slightly or not at all at the temperature of most rapid action during the time of temperature drop. This point will become more apparent as the results are examined.

Estimating Progress of Transformation

When steel transforms, a number of properties are changed. One important property that is radically changed is the magnetic permeability. While the permeability is somewhat different among the products of the austenitic transformation at different temperatures, yet the order of magnitude of the permeability is entirely different as between austenite and the products of transformation. Therefore the decrease in austenite and increase in ferrite could be evaluated by observing the increase in permeability as the reaction proceeded. This method was actually utilized in somewhat similar work.[5] Volume changes also occur, which are characteristic for the austenite to ferrite change. Hence buoyancy evaluations might be continuously registered as the specimen undergoes change in the metal bath. Characteristic hardness changes result from transformation and, while somewhat complex, could be used to evaluate the progress of the transformation. In this case indentations with a uniform pressure might be made in the specimen at intervals and their depth interpreted later.

On the basis of practicability, two methods were used to estimate the progress of the reaction, one for the higher constant temperatures and another for the lower. Both methods were employed for some intermediate temperatures, providing thereby a check on their accuracy.

So far as temperatures from the lower critical (eutectoid) down to about 300° C. (570° F.) are concerned, the progress of transformation may be followed by a method of considerable dependability and directness. It depends upon subsequent microscopic examination and therefore may be carried out deliberately with no necessity of continued obser-

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[5] D. Lewis: *Loc. cit.*

vations of any manifestation at frequent intervals. By preparing a considerable number of small specimens the distribution and extent of austenite remaining after any length of time can be rigidly fixed and preserved for later evaluation. While austenite transforms to characteristic martensite upon quenching rapidly into a bath of cold water, it never forms martensite when it transforms in the temperature range down to 300° C. (570° F.), producing, instead, some form of pearlite or troostite. Hence, if a series of small specimens are quenched to the desired temperature in the molten metal bath and then, one by one, at suitable time intervals are removed quickly and quenched into water, the austenite unchanged at intermediate temperature will be fixed and preserved as martensite. Subsequent microscopic examination will then reveal in sharp contrast the progressive loss in austenite and gain in transformation products. The utterly different etching characteristics of martensite and the products of elevated temperature transformation serve to permit the most definite sort of area estimation. Such a series of specimens shows, for the short time in the bath of observation temperature, pure martensite, and for the very long times, pure pearlite or troostite, as the case may be. Intermediate times result in the expected mixtures in adequately sized areas for accurate planimetric estimation.

The specimens removed from the intermediate bath prior to any transformation are, incidentally, fully hard after the water quench (i. e., Rockwell 56 to 65, depending upon composition) whereas those removed to the water after considerable transformation has occurred are increasingly soft, reaching finally the normal hardness of the transformation product. Thus both hardness and structure furnish a clue to the procedure of the decomposition of austenite.

The second method used for the lower temperatures depends upon the increase in volume of any steel upon transformation to troostite or martensite as reflected by length change. The authors are aware not only that volume changes are slightly affected by shape of specimen but also that the volume change is not necessarily uniformly reflected in linear change in all dimensions. Indeed, the thickness of flat disk specimens actually decreases with volume increase! However, it has been established satisfactorily that length changes in long slender specimens of constant cross-section follow reasonably closely the transformation in the course of expansion. The method is not so precise in terms of quantitative estimation as the first method, but indicates with considerable fidelity the inauguration and completion of the transformation. The checking of the expansion against the microscopic appearance at intermediate temperatures provided evidence of excellent agreement in all steels save one (steel B) and even there the discrepancy was not serious.

To carry out the method of employing length change to indicate continuously the progress of transformation, some skill and dexterity is

required. The hot specimen, heated to dissolve the carbide completely, must be removed from the furnace with heated tongs, attached to the dilatometer and immersed in the bath before proeutectoid constituents have time to separate or any decomposition occurs as a result of the slight air cooling, which, of course, is unpreventable. Frequent tests showed that this was accomplished in these investigations. (It will be seen that the time of appearance of the proeutectoid constituent was observed and recorded.)

The dilatometer used is illustrated in Fig. 2. It is similar to the one used by Bain and Waring[6] and by Grossmann,[7] but an extra precaution was necessary. The dial readings actually represent only the difference in expansion between the dilatometer fittings and the specimen. To ensure the accuracy of the expansion values it is necessary to reduce the length change in the dilatometer side rods substantially to zero. This was accomplished by holding the dilatometer in the molten metal bath until it was in thermal equilibrium (i. e., conducting away heat at a constant rate and with a constant thermal gradient existing). For inserting the specimen the dilatometer was raised in the bath momentarily and then replaced before significant temperature changes resulted. The more nearly the specimen retained the furnace temperature and the more nearly the dilatometer retained the thermal conditions set up by the bath, the more immediately and accurately would the dial readings reflect the true conditions in the specimen. As already stated, the instances wherein the steel began transforming within 2 or 3 sec. probably are not without some slight error.
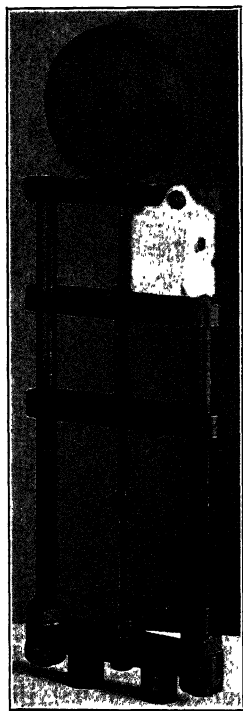
FIG. 2.—THE QUENCHING DILATOMETER.

In quenching the specimens to temperatures below the freezing point of the lead-bismuth bath, a large volume of water was used at 71° C. (160°F.) and at 15° C. (60° F.). The transformation time, or at least the time for substantially complete transformation at such low temperatures, is too short to be measured very accurately. It has been shown that not only is some austenite retained permanently after low-temperature quenches, but that the last traces of austenite to transform under such conditions do so at an extremely slow rate. This paper does

[6] E. C. Bain and W. S. N. Waring: Austenite Decomposition and Length Changes in Steel. *Trans.* Amer. Soc. Steel Treat. (1929) **15**, 69.

[7] M. A. Grossmann: Discussion of paper by Bain and Waring. *Ibid.*, 90.

not concern such behaviors of the last traces, but confines itself to the estimation of the major portion of the austenite, which does transform. It is believed that the apparent end of reaction time as observed here represents the transformation of about 99.5 per cent. of the austenite undergoing transformation (exclusive of that retained ·permanently).

It has already been pointed out that the specimens must be introduced into the dilatometer and then submerged into the quenching bath very quickly. To aid in accomplishing this, each end of the specimen was broadly notched and these polished notches engaged similar notches in the fixed and movable part of the dilatometer set at right angles to the flat specimen (Fig. 3). In a sense, therefore, the specimen was self-aligning. The relation of the specimen to the seats in the dilatometer at the point of engagement was actually similar to that of adjacent links in a simple chain. Precision of the readings was improved by attaching a small vibrator to the dilatometer. The vibrator consisted of a signal buzzer operated from a battery (Fig. 2).
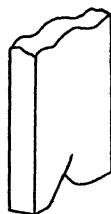
STEELS CHOSEN FOR STUDY

The steels chosen for study were representative materials of low alloy content and of an intermediate content of manganese; they form a variable carbon series and a manganese series. A typical high-carbon steel with a little chromium, such as that used in razor-blade strip, also was investigated. To present one example of a high-alloy material, standard stainless cutlery steel was explored in a somewhat less detailed manner.
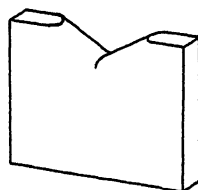
FIG. 3.—ENGAGE-MENT OF SPECIMEN IN DILATOMETER SEATS.

The analyses of the seven steels investigated are given in Table 1.

TABLE 1.—*Analyses of Steels Investigated*

Steel[a]	Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Sulfur, Per Cent.	Phosphorus, Per Cent.	Chromium, Per Cent.
A	1.13	0.30	0.171	0.015	0.026	
B	0.78	0.36	0.160	0.048	0.036	
C	0.54	0.46	0.198	0.041	0.048	
D	0.50	0.91	0.131	0.041	0.046	
E	0.64	1.13	0.094	0.030	0.048	
F	1.17	0.30	0.180	0.033	0.026	0.26
G	0.35–0.40					12–14

[a] Steels A, B and C constitute the carbon series; C, D and E constitute the manganese series; F is a razor-blade steel and G is cutlery stainless steel.

Steel B was studied more minutely than any of the others. In the course of observing its behavior at many temperatures selected at close

intervals, not only was skill and experience acquired but the general trends of the temperature effect were observed in sufficient detail to warrant reducing the number of temperatures selected for investigating the other steels. The study of this steel involved 152 separate microscopic examinations and the plotting of 13 expansion curves. It would not have been practicable to examine all the steels in such detail.

⸱ RESULTS OF INVESTIGATIONS

The behaviors investigated may be designated as

1. Time involved in transformation.

2. Hardness of the products as influenced by temperature of transformation.

3. Structures resulting from transformation at the various temperature ranges.

4. Effect of carbon and alloys upon transformation time.

5. Retention of austenite at lower temperature ranges.

Time Required for Transformation

As outlined above, the progress of the transformation was followed by two methods. When the microscopic appearance was used as the method of estimation the nature of the product was simultaneously observable. In this case enough specimens were employed to give some definite notion of the velocity of the reaction at different times. By interpolation the time required for certain definite fractions of the austenite to transform was estimated. The direct evidence from the specimens held in the molten bath for different lengths of time was recorded in terms of the percentage of austenite unchanged, pearlite or troostite already formed and proeutectoid constituents, if any. Subsequently this information was condensed graphically by the use of symbols (Fig. 14) in circles located on a time-temperature system of coordinates. Fig. 4 shows such a chart subsequently discussed in detail.

Carrying out the expansion method involved plotting the time-length change curves. The total expansion that occurred was taken to correspond with complete transformation and the times required to permit definite fractions of this total expansion were read off this graph as the time of fractional conversion of austenite. In this manner the expansion data at low temperatures were secured and plotted (as in the lower portion of Fig. 4) as derived from a family of expansion curves like that shown in Fig. 5. It might be pointed out that the bands of increasing width of Fig. 4 are plotted to a definite scale of expansion and represent the beginning of the transformation, the 25 per cent. transformation, the 50 per cent., the 75 per cent. and the concluded transformation as evidenced by the expansion.

From such charts as the one in Fig. 4 were prepared the summary curves for the various steels, Figs. 6 to 12 inclusive. All the data, in detail,

from which the summaries were prepared are shown only for steel B, it being assumed that the chief interest lies in the summary and the inclusion of so many charts would require too much space.

It should be mentioned, perhaps, that there is necessarily some vagueness concerning the exact instant of the beginning of the transformation and its end. (In all probability the curves of all such processes may actually be asymptotic at the conclusion.) It may be said,
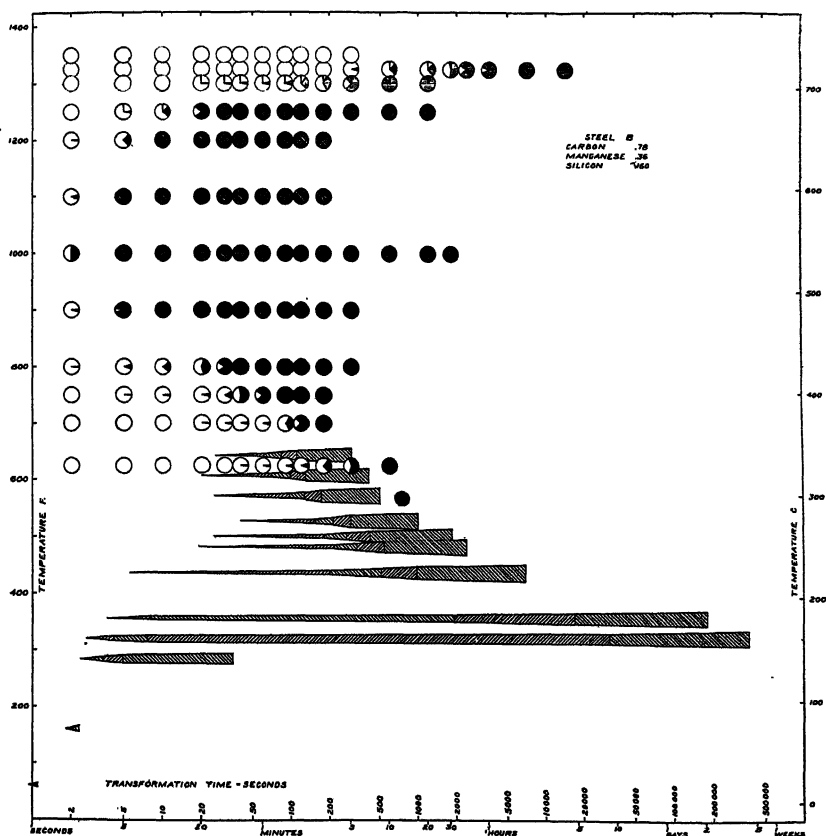
Fig. 4.—Typical data chart for transformation time and structure (steel B)

however, that the time point selected as representing the inauguration of the transformation marks the decomposition of less than 0.5 per cent. of the austenite, and that the time indicated as the end of the transformation designates that not more than 0.5 per cent. of the ultimately transforming austenite remains.

In the case of steels of composition remote from the eutectoid, the proeutectoid constituent separates out at subcritical temperatures: but only at temperatures a few hundred degrees Fahrenheit below the critical. At temperatures below this range, this does not occur. The time of this

proeutectoid separation is shown for the hypoeutectoid steels; the actual estimation of proeutectoid carbide is less easily made, and is not shown. In all cases, the lower the temperature of the transformation the smaller is the volume of excess constituent (ferrite or carbide) precipitated prior to the general decomposition.

It may be regarded as unfortunate that the abscissas of the various charts show time on a logarithmic scale. Actually this is practically
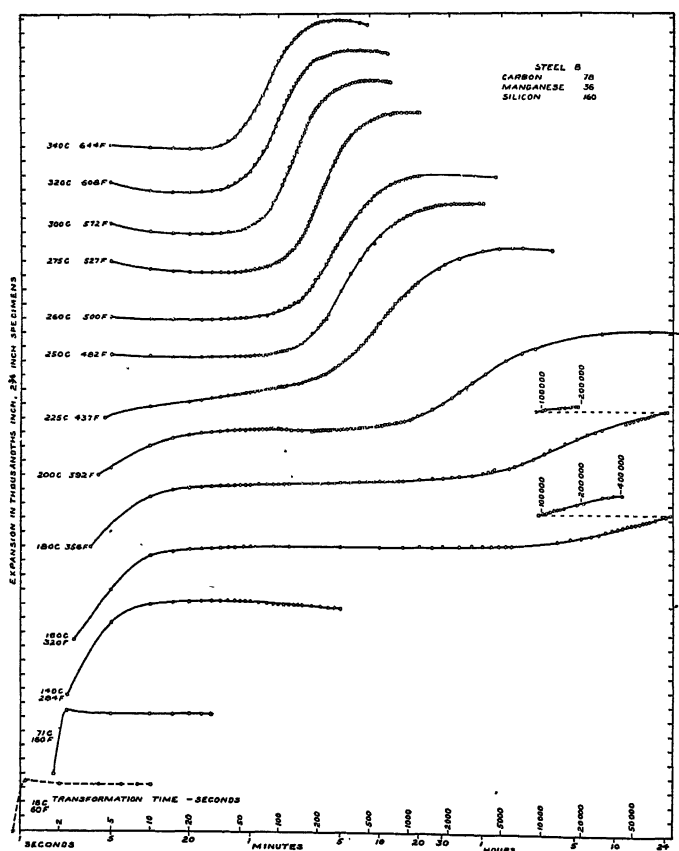
FIG. 5.—EXPANSION CURVES FOR STEEL B.

unavoidable because of the great disparity in rates of transformation at the various temperatures. Indeed, the transformation may require over 100,000 times as long an interval at the temperature range of slow action as at the temperatures of rapid reaction. If a linear scale were adopted, obviously no detail could be shown in the short time intervals.

For all the steels the transformation time graphs (Figs. 6 to 12) take the roughly approximate form of S-shaped curves. This circumstance is seemingly highly characteristic of all hardenable steels. The precise

location of the S curve depends upon composition, but even the high
alloy steel shows the same trend.   There are two temperature ranges of
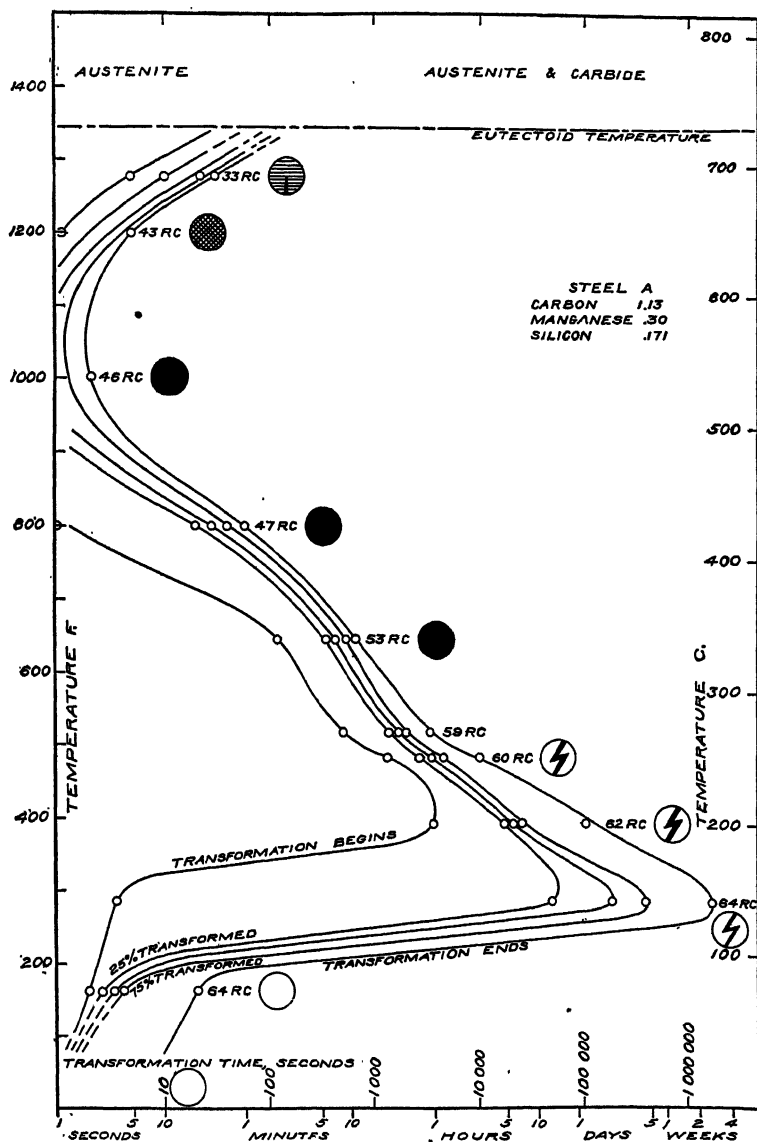
FIG. 6.—SUMMARY CHART FOR STEEL A.

very rapid transformation; one at about 550° to 600° C. (1000° to 1100°
F.) and the other at low temperature not exceeding about 150° C. (300°
F.).   For high-alloy steels these ranges may be somewhat different,
depending again upon composition.   This circumstance of the two

ranges of rapid transformation throws new light upon the significance of the so-called A' and A" points. Strictly speaking, there are no actual
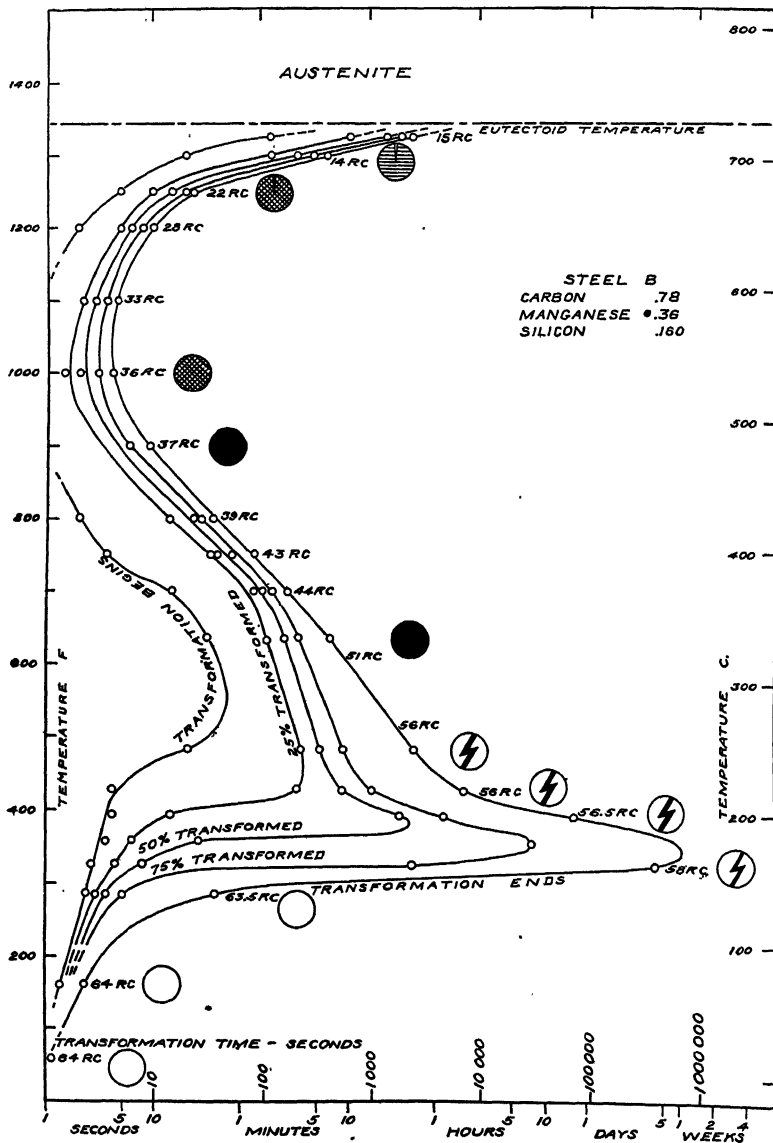
FIG. 7.—SUMMARY CHART FOR STEEL B.

"points," but with any cooling at moderate rate the metal will be in the upper range of high transformation velocity sufficiently long to transform; if, however, the quenching rate is sufficiently high to cool the steel through this range unchanged, then so slow is the reaction at the next

lower temperature range that in general the austenite must reach the *second* region of high transformation velocity, there to transform in a different manner. Obviously, certain rates of cooling will permit a
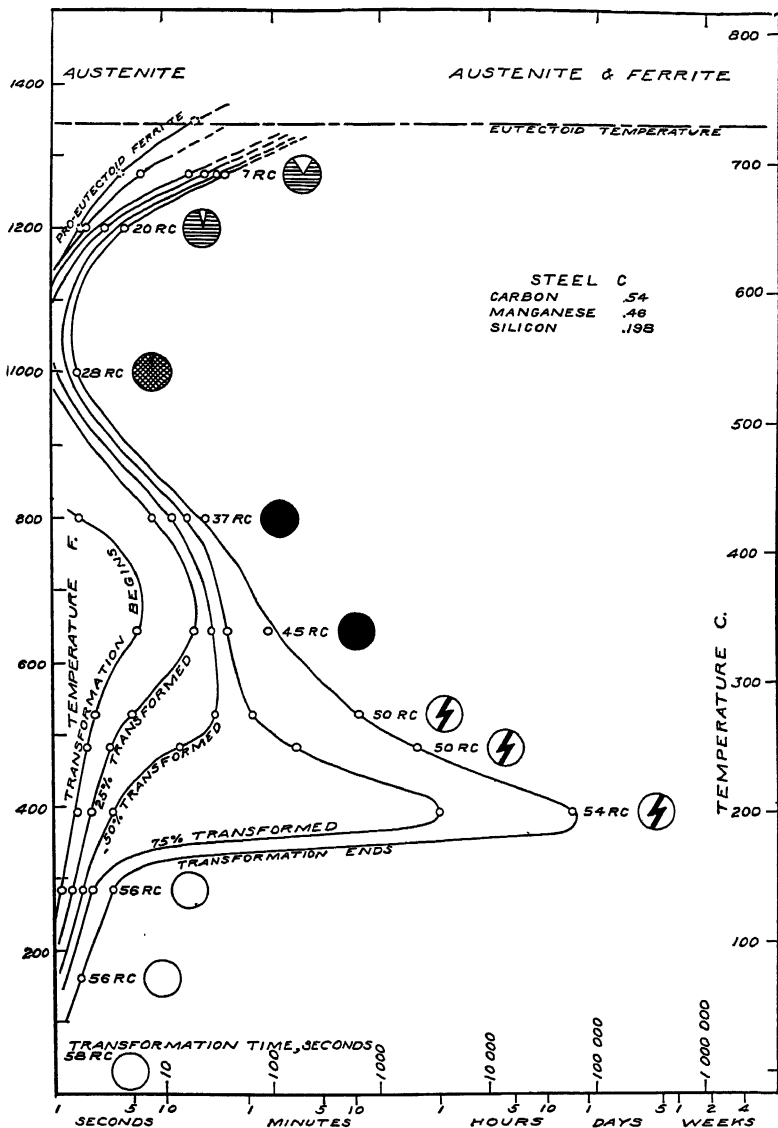
FIG. 8.—SUMMARY CHART FOR STEEL C.

portion of the austenite to transform (the innermost region, for example) at A' and the remainder will only react at A''. The "split" transformation takes on a definite significance in the light of these rates of transformation at constant temperatures.

It seems more than probable that the transformation time for certain high-alloy steels that harden completely in oil or air may be infinitely
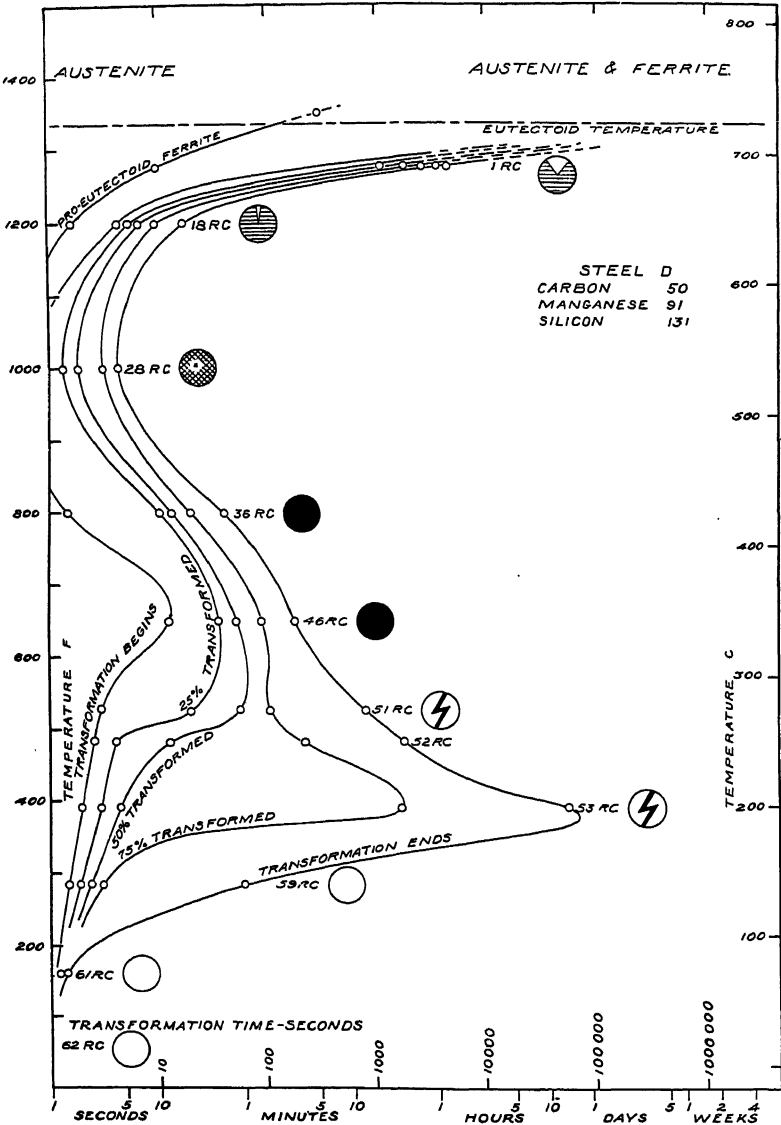
FIG. 9.—SUMMARY CHART FOR STEEL D.

long at certain temperatures. At any rate, nearly a month at 200° C. (390° F.) caused only a beginning of transformation of the austenite of the stainless cutlery steel G, although the specimen when cooled to about 100° C. (200° F.) hardened thereafter almost instantly to full hardness value. In this connection it is interesting to read the paper by DeLong

and Palmer[8] on what happens when high-speed steel is quenched and the discussion which the paper called forth.
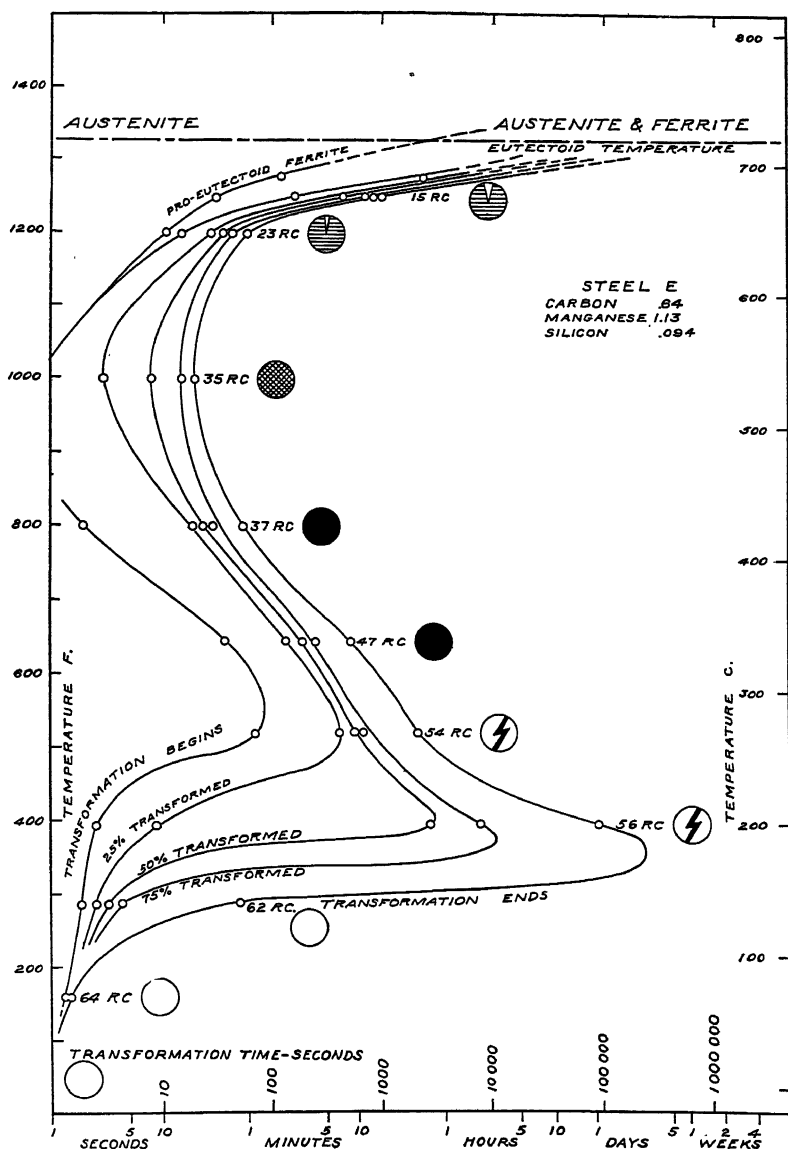
FIG. 10.—SUMMARY CHART FOR STEEL E.

In the range of temperature from the eutectoid down to about 500° C. (930° F.) the time of transformation appears to decrease with either increasing or decreasing carbon as it departs from the eutectoid

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[8] B. H. DeLong and F. R. Palmer: *Loc. cit.*

composition, which appears to be the most sluggish toward change. In this range of temperature, manganese retards the reaction markedly.
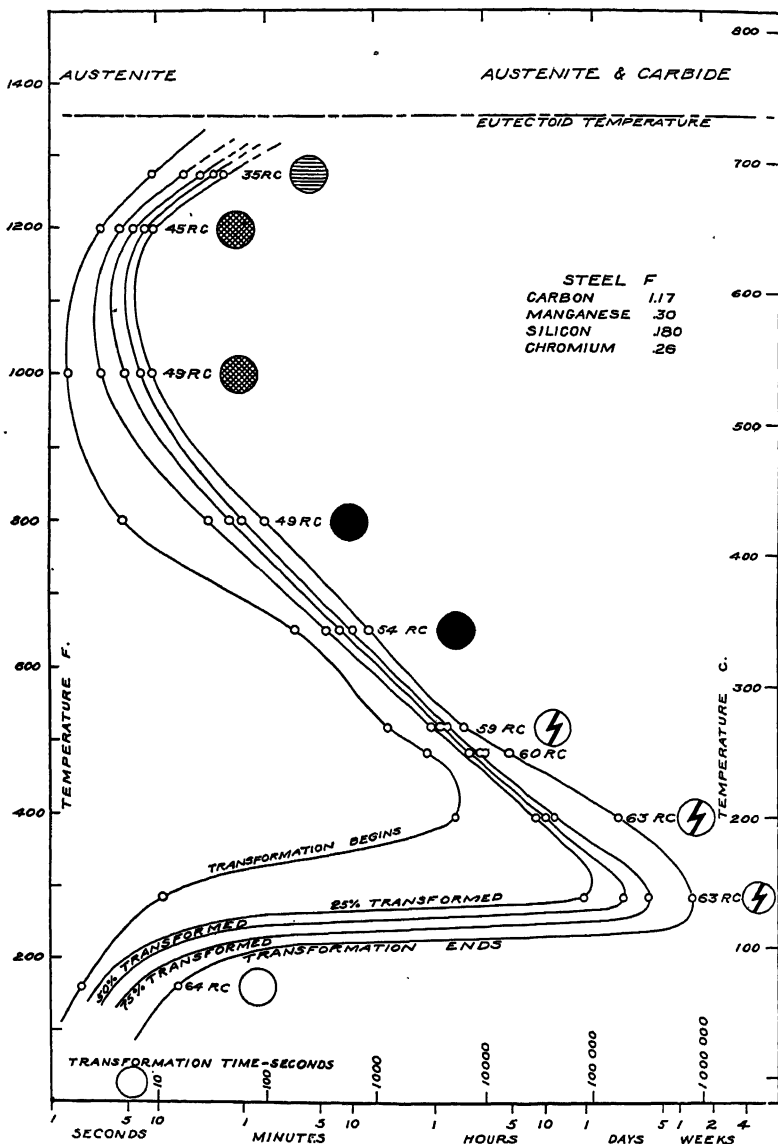
FIG. 11.—SUMMARY CHART FOR STEEL F.

At the lower temperatures of transformation both carbon and manganese have the definite effect of decreasing the rate of transformation. This effect is particularly evident in the time required for the

beginning of the reaction. The temperature of maximum time lag prior to incipient transformation is lowered both by carbon and manganese.

STEEL G
CARBON   .35 - .40
CHROMIUM   12 - 14
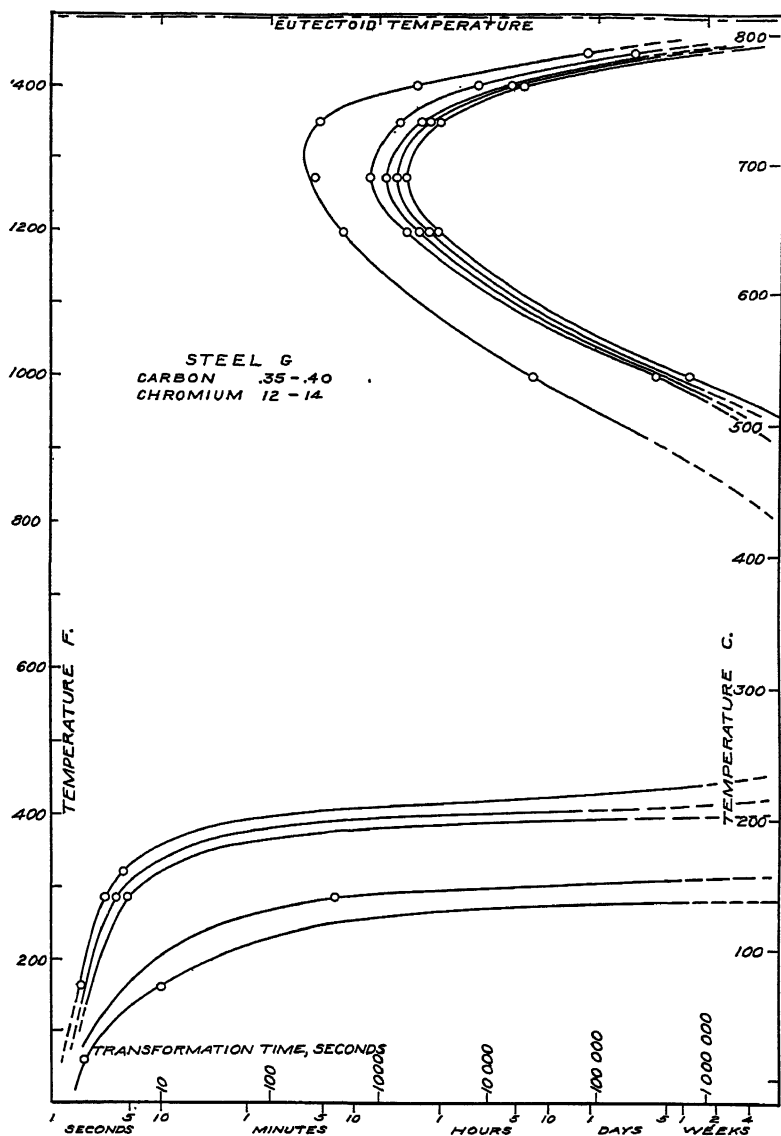
FIG. 12.—SUMMARY CHART FOR STEEL G.

Even the small amount (0.26 per cent.) of chromium present in steel F seems by comparison with steel A to retard the reaction of the austenite, especially at elevated temperatures where the transformation is most rapid. Fig. 12, of the stainless steel G, shows how the S-type curve

actually persists even when the chromium has caused the steel to become so sluggish as to render its study entirely impractical in some ranges. In determining the severity of practical quench necessary for hardening a steel, the maximum rate of transformation that occurs at 600° to 700° C. (1100° to 1300° F.) is the real criterion. Once the metal cools below this temperature range, it is most likely to harden upon subsequent cooling. It is apparent, therefore, that steel G should be an air-hardening steel.

Hardness of the Transformation Products

The curves of Fig. 13 show the hardness (at room temperature) of the various transformation products of the several steels as developed over
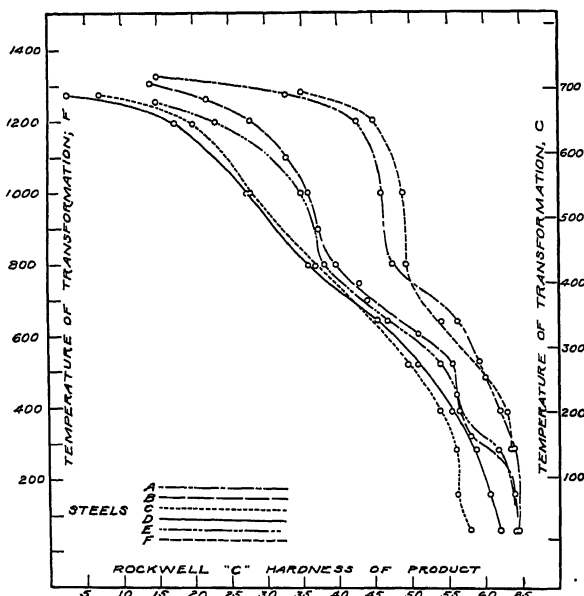
FIG. 13.—ROCKWELL HARDNESS OF COMPLETED TRANSFORMATION PRODUCTS.

the entire temperature range. As would be expected, the lower transformation temperatures produce structures that are greatly harder than the products from higher temperature of transformation. The hardness does not vary uniformly with the temperature of the action, but seems to vary in a characteristic manner. This may be explained on the basis of the time effect. Thus, when the transformation is very slow, the first austenite to transform is subjected to the drawing or tempering action of the bath over the entire time required for the last fragments of austenite to react. Hence we should find disproportionate softness in the products from temperatures of slow transformation and comparatively greater hardness in the product that transformed rapidly. A comparison of the

hardness curves (Fig. 13) with the summary curves will show the existence of this relationship.

It is important to bear in mind that the figures as plotted on the hardness curves (Fig. 13) and as noted on the summary charts are representative of the hardness of the product of the *just-completed* transformation. The hardness of any actual specimen permitted to remain in the molten bath after the austenite has completed its transformation will gradually fall, on account of coalescence of the carbide. The lamellar pearlite gradually spheroidizes and the products of finer carbide distribution similarly coalesce at rates depending upon the temperature. This action is slow in comparison with the rate of the decomposition of austenite at higher temperatures.

In this connection it may be well to mention that the hardness of the successively water-quenched microscopic specimens withdrawn from the metal bath at intervals constitutes also an excellent check on the microscopic estimation of the progress of the decomposition of the austenite. Specimens removed from the transforming temperature bath and quenched in water before much action has occurred possess nearly full martensitic hardness. Those removed after the transformation has occurred are, as would be expected, very much softer.

A set of such hardness curves with hardness plotted against time at constant temperature was made for each steel studied. The transformation time may almost be read from these curves alone.

Structures Resulting from Transformation at Various Temperatures

A discussion of structures in steels almost unavoidably involves the use of certain well established names, which have their origin in microscopic appearances. That these names are difficult to assign in the present specific cases arises from a number of circumstances, some of which are general and some of which apply particularly to the present study. The structure as studied in the microscope is merely the appearance of a metallic surface after the devastation of an acid corrosion attack has occurred. Under vertical illumination the gradation of reflecting power of such surfaces from point to point depends upon a variety of circumstances not well understood. Where two or more phases of resolvable dimensions are present, the inferences may be drawn with some assurance, but when such conditions do not obtain (as with all low-temperature transformations in steel) the nature of the structure must remain obscure after microscopic examination. In spite of this undeniable physical consideration, the authors have attempted to follow the custom and to name the structures found in accordance with the traditional conventions.

Some of the types of ferrite-carbide association obtained by the present heat treatments do not fit in well with the usual martensite-

troostite-sorbite-pearlite series. In accord with the suggestions made by both Hoyt and Sauveur,[9] the name sorbite has not been used at all. For many years the authors have believed that the "nodular troostite" developed by quenching at an intermediate rate was actually fine pearlite. Since the presentation by Lucas[10] of a similar view, it seems clear that the product of transformation at the constant temperature which forms this particular microscopic appearance should be called pearlite, or more specifically, fine pearlite.

The etching characteristics of several zones of quenching temperatures can actually be recognized after some practice, but it has seemed sufficient to name all the entirely unresolvable,[11] dark-etching products "troostite." The completed transformations forming troostite always possess the extremely rapid and dark-etching characteristics but vary somewhat in appearance with the temperature of formation and carbon content. A soft and vague acicular aspect may be seen with light etch, but the rate of attack (e. g., in 2 per cent. alcoholic nitric acid) alone would suffice to differentiate this constituent.

PRO - EUTECTOID ADMIXTURES

TOP - FERRITE
BOTTOM - CARBIDE

PEARLITE

FINE PEARLITE

TROOSTITE

MARTENSITE-TROOSTITE

MARTENSITE

FIG. 14.—SYMBOLS USED TO DESIGNATE STRUCTURES ON ALL CHARTS.

At lower transformation temperatures the product etches more slowly and the darker needles are clean-cut and definitely acicular. Even here, however, a brownish coloration shows that the product is not true martensite. To specimens of this intermediate appearance the name martensite-troostite has been given for convenience. When the slowest-etching acicular state of affairs was evidenced, the name martensite was used. Actually, if an extraordinarily severe etch is applied to a truly martensitic specimen, the final appearance is somewhat similar to that of the martensite-troostite group, but even then experience would enable one to distinguish between the two. It was most satisfactory to etch an entire series in a holder at one time, so that the conditions for all were identical as to time, temperature, etc. The authors wished to use numbers or letters to designate products of transformation but this seemed still more artificial and tedious for the reader and accordingly

[9] S. L. Hoyt: Metallography. Pt. 2. Metals and Common Alloys. New York, 1920–21. McGraw-Hill Book Co.

A. Sauveur: The Metallography and Heat Treatment of Iron and Steel. New York, 1926. McGraw-Hill Book Co.

[10] F. F. Lucas: Structure and Nature of Troostite. *Bell System Tech. Jnl.* (1930) 9, 101.

[11] Unresolvable so far as individual carbide particles are concerned.

this attempt to adhere both to fact and convention was decided upon. It is suggested that the reader substitute for the names used here any that he finds more convenient for the structures designated. No defence for the present names is offered other than that of expediency. The names chosen by the authors are as follows; the symbols are shown in Fig. 14:

1. Pearlite—easily resolvable lamellar carbide-ferrite eutectoid structure.

2. Fine pearlite—lamellar eutectoid structure resolvable only at highest powers, which forms by the nodular process.

3. Troostite—dark-etching unresolvable appearance, which forms by somewhat acicular development and not by radial or nodular growth.

4. Martensite-troostite—the structure that forms by distinct acicular procedure and retains acicular markings, but etches much more rapidly than martensite and less rapidly than troostite.

5. Martensite—the structure of full-hard quenched steel, which etches slowly and shows acicular markings. By virtue of its slow attack it is always brilliant white by contrast with the other products of transformation.

The typical appearance of the end products of austenite transformation are shown in Figs. 15, 17, 19, 21 and 22. In the order mentioned they are of pearlite, fine pearlite, troostite, martensite-troostite at its lowest temperature range (just distinguishable from martensite) and martensite-troostite at the highest range of formation. To illustrate more clearly the mode of development of the first three constituents, photomicrographs of the same constituents as partly transformed from austenite are also included. Opposite the corresponding photomicrographs of completed transformation products will be found Figs. 16, 18 and 20, showing the partly transformed austenite resulting from the interruption of the transformation at an intermediate stage. Actually the white background of the photomicrographs is martensite but was austenite at the moment of the quench from the lead bath into water. The specimens were deliberately etched so as to show no detail in the background, thereby simulating more nearly the ideal conditions, which would obtain if one could observe the transformation as progressing at the temperature of transformation. Fig. 22, of the martensite-troostite constituent transformed at the highest part of this temperature zone, resembles more closely the pure troostite, whereas the structure of Fig. 21 is very near that of true martensite. However, the etching rate is sufficiently different from that of martensite to warrant a different classification.

To illustrate further the basis for naming as fine pearlite that certain constituent which forms by nodule growth with roughly radial markings, Figs. 23 and 24 are introduced. These photomicrographs were made at about the limit of resolution of the microscope ($\times$ 2500) and show clearly

Fig. 15.—Typical pearlite. × 500.
Fig. 16.—Pearlite partly formed. × 500.
Fig. 17.—Typical fine pearlite. × 500.
Fig. 18.—Fine pearlite partly formed. × 500.
Fig. 19.—Typical troostite. × 500.
Fig. 20.—Troostite partly formed. × 500.

the distinctly lamellar characteristics of the product. Each figure shows a large proportion of this clearly lamellar condition and even the remainder suggests this condition, as though the plane of the polished section had been too nearly normal to the lamellae to offer sufficient separation in the traces.

As has been pointed out earlier, at temperatures a few hundred degrees below the eutectoid, the transformation of the austenite is preceded by a separation of proeutectoid constituent if the composition of the steel is somewhat removed from the eutectoid carbon content. The magnitude of the proeutectoid constituent becomes less as the constant temperature of transformation falls lower, until at about 593° C. (1100° F.) no more ferrite or carbide separates and the steel transforms as a whole. In
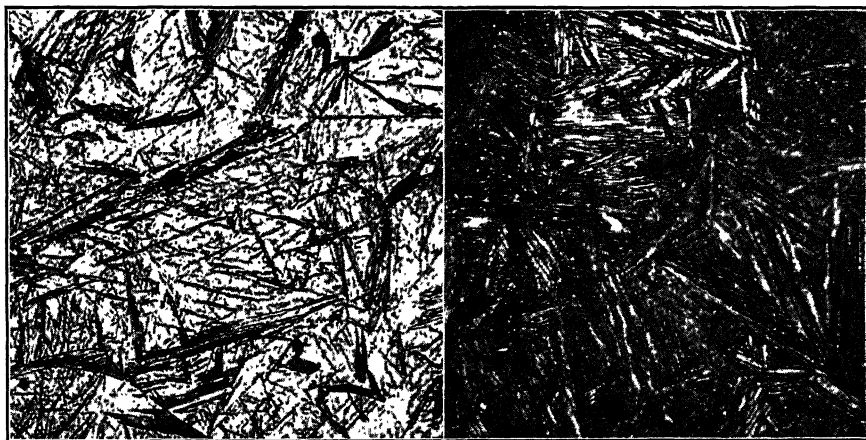
FIG. 21.—MARTENSITE-TROOSTITE, LOW RANGE. × 500.   FIG. 22.—MARTENSITE-TROOSTITE, HIGH RANGE. × 500.

Figs. 25 and 26 are shown the structures of a hypoeutectoid and hypereutectoid steel, respectively, as held for some time just below the critical temperature and then quenched. The constituent marking out austenite grain boundaries in the hypoeutectoid steel is ferrite and in the hypereutectoid steel it is carbide. The quenching here took place at a time to prevent the formation of pearlite in the high-carbon steel, while Fig. 25 shows the transformation as having progressed sufficiently to form some pearlite. As a matter of fact, even substantially below the lower critical temperature, the reactions appear to take place somewhat normally in that no further proeutectoid constituent separates after the eutectoid transformation begins, regardless of the amount of the constituent separated.

No photomicrographs of martensite are shown here; the appearance was precisely that of the hundreds of etched martensite photographs shown in many publications.

Fig. 23.—Fine pearlite. × 3000.
Fig. 24.—Fine pearlite. × 3000.

It may be well to point out some of the characteristic differences between the transformation products of hypereutectoid and hypoeutectoid steels, although it must be admitted that the outstanding characteristic of the structures is their general similarity. Except in respect to the proeutectoid material, no significant difference exists between the pearlite and fine pearlite of the two classes of steels. In the formation of troostite there is one difference, which is marked. The troostite of low-carbon steels forms by the development of more distinctly rectilinear markings; the high-carbon troostite is less acicular and more ragged. These tendencies are most easily recognized in the partly transformed material
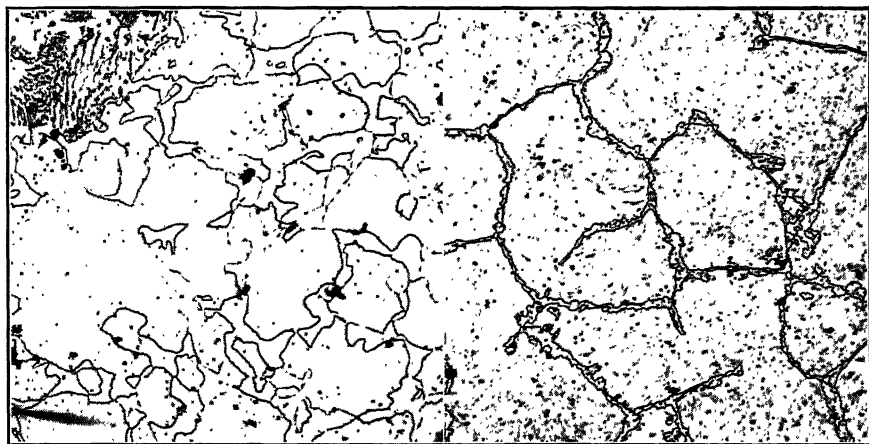
FIG. 25.—PROEUTECTOID FERRITE.   FIG. 26.—PROEUTECTOID CARBIDE.
              × 500.   × 500.

but would not be overlooked even in the finished product. The photomicrographs shown are probably slightly more characteristic of high-carbon material than of the low-carbon.

In the formation of the product designated here as martensite-troostite, the tendencies described for troostite are practically reversed. The dark-etching "needles" are more perfectly rectilinear and more sharply defined in the higher carbon steels. The manganese content has surprisingly little effect upon the appearance of the transformation products.

In the investigation, some 600 specimens were examined microscopically, but it is believed that the 12 structures shown here are sufficiently representative to give an adequate survey of the effect of temperature of transformation upon the structure of the product. Furthermore, since the inauguration of this investigation, a publication

by Robertson[12] has treated the microstructural aspects of a similar study in an excellent manner.

Retained Austenite

Under the heading Time Required for Transformation, the fact was stressed that the discussion of rates of decomposition of austenite did not deal with permanently retained austenite nor even with any austenitic transformation that was occurring so slowly that no measurable expansion was incurred in a few days at constant temperature. It seemed important, nevertheless, to estimate by means of the X-rays the conditions under which austenite was retained after transformation had appeared to cease. Such an estimation may not be carried out accurately, it is found, because martensite or martensite-troostite produces an X-ray diffraction pattern of such diffuseness as to make intensity comparison with the sharper austenite pattern very difficult. Still, some fair approximation may be made. In brief, the deductions are as follows:

1. No austenite was found in the products of transformation at temperatures above 180° C. (356° F.) in any steel.

2. Steel B retained a trace of austenite after transformation at 180° C. (356° F.) but the other steels contained no austenite unless they transformed at temperatures of 140° C. (284° F.) or below.

3. The amount of austenite retained was perhaps greatest after the water quench at 16° C. (60° F.) but very little more was retained than after the quench into water at 71° C. (160° F.); at higher constant temperatures the amount fell off rapidly.

4. The amount of austenite retained increased rapidly with carbon content, reaching about 20 or 25 per cent. in the high-carbon steels A and F and amounting only to a trace in steel C of low carbon content (0.54 per cent.).

5. Austenite may be definitely retained permanently in steels in which the ultimate transformation product is not martensite but one of the softer martensite-troostite structures.

6. The stainless cutlery steel, for all its great sluggishness, retained far less austenite than the high-carbon steel, presumably because of its low carbon content (0.35 per cent.). Carbon ranging from 0.50 to 1.20 per cent. is far more effective in increasing retained austenite than manganese ranging from 0.46 to 1.13 per cent.

DISCUSSION OF RESULTS

The C-shaped curves for all steels resulting from plotting temperature of transformation (between eutectoid temperature and that of maximum time) against time required may be predicted from purely

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[12] J. M. Robertson: The Microstructure of Rapidly Cooled Steel. *Jnl.* Iron and Steel Inst. (1929) **119**, 391.

physical-chemical considerations. The reaction time for transformation may be regarded as the summation of the time factors of two essential effects, "tendency" or "driving force" and ease of transformation or "facility," neither of which is linear with temperature. The former would tend to decrease the time rapidly at first with falling temperature, then more slowly. The other would tend to hold the time short at the temperature near the critical but to increase it enormously at lower temperature ranges. Obviously, the mutual effect would cause the typical minimum observed in the vicinity of 540° C. (1000° F.). The second temperature of rapid transformation must be explained on the basis of some other consideration. There is no lack of sufficient differences in the nature of transformations at room temperature or thereabouts from which to construct theories. The two most entertaining ones are probably the negative "ferrostatic" pressure, which a *hard* surface product might set up to catalyze the reaction, and the fact that martensite, the product of low-temperature transformation, is one in which no carbon diffusion or migration takes place.

Considering the first, it might be reasoned that the softer products of the long-time transformation in which carbon may easily precipitate lacks hardness and strength to exert during its expansion any great outward force in all directions while a harder, low-temperature product could well accomplish this. Such a negative pressure would certainly aid the transformation of austenite, since by its transformations it expands considerably. Such autoaccelerating effects are found in other cases. It might be reasoned, in the second theory, that the time-consuming part of transformation is the carbide precipitation incurred thereby and if this could be eliminated wholly or in part the mere allotropic transformation could proceed very rapidly, since it involves only a slight atomic rearrangement essentially *in situ*. Since martensite has essentially all the carbon held in unstable solid solution, the migration of carbon is avoided and the change can be almost instantaneous. Possibly both theories bear upon the subject.

At any rate, an inspection of the structures resulting from transformation over the temperature range indicates clearly that at elevated temperatures the carbide precipitation is not lagging far behind the allotropic change at any point. As the temperature of transformation is lowered, the tendency for the alternate, and hence simultaneous, separation of carbide and ferrite disappears and instead the trend of the allotropic change to sweep across a grain ahead of carbide separation becomes more and more marked down to the martensite reaction. A logical intermediate case would be the fine pearlite of nodular origin proceeding from a comparatively few nuclei. In forming troostite, the allotropic change would occur just a little in advance of the carbide precipitation—enough to produce the "needles" or bars across the

austenite grains. This trend seems to grow stronger and stronger with lowered temperature, until finally in martensite little if any carbide ever separates.

The authors suspect that the final constituent designated as martensite-troostite first forms much in the manner of martensite but is subsequently more or less tempered and succeeds in precipitating carbon, depending upon how long the restricted area under consideration remained at the constant temperature. This is borne out by the similarity of some of these structures to those of lightly tempered pure martensite. The tendency toward a light gray (or brown) etching effect also suggests slight carbide precipitation subsequent to the allotropic change.

The length of time required for transformation over a considerable range of temperature was surprisingly long. The products of transformation at some of these unusual temperatures possess desirable physical properties. It is important, however, that steel thus treated be not withdrawn prematurely from the bath temperature to finish transformation at a rapidly falling temperature, for the austenite remaining will then transform wholly or in part to martensite, the admixture of which will impair some of the physical properties of the metal. In general, it is far better to raise the temperature and maintain it long enough to make certain that complete transformation at the more rapid rate has occurred.

The transformation rate for some of the high-alloy tool steels is so low that they may be retained almost indefinitely at certain temperature ranges in the austenitic condition. Apparently the temperature of slowest transformation is the one at which carbide will just barely precipitate from the quenched steel upon reheating.

ACKNOWLEDGMENTS

DISCUSSION

M. A. GROSSMANN, Canton, Ohio.—This brilliant paper clarifies many of our ideas on the hardening of steel. Certainly it brings in new conceptions of the Ar' and Ar'' points, the transformations at the upper and lower temperatures below the critical.

The program notes this as a session on theoretical metallurgy, but I think we should bear in mind that this has very important practical aspects also. When we consider that the quenching of a piece of steel into a bath at 250° degrees, or a bath at 200°, requires in the one case some two weeks for the transformation of the steel, as shown by the authors, and in the other case a fraction of a minute, I think we can see that this has very important bearing on all of our heat-treating operations, and also our conceptions of these operations.

D. J. Demorest, Columbus, Ohio.—I have had more clarification of my mind this afternoon, as a result of this paper by Messrs. Davenport and Bain about the processes of hardening, than from anything I have ever read before.

F. B. Foley, Philadelphia, Pa. (written discussion).—The authors of this paper are to be congratulated for their technique and for their clear presentation of the results of this study of a rather elusive problem. It immediately brings to my mind the work on critical rates of cooling by Portevin and Garvin and also the work of French and Klopsch. It shows that the microconstituents of steels cooled from above the critical temperature are all direct decomposition products of austenite and not successive derivations of austenite through a series of transformations involving the traditional descent through martensite, then troostite, then sorbite, and, finally, pearlite. This latter series of transformations is produced in reheating austenite or martensite and is therefore identified with drawing or tempering. Two interpretations were possible of the split transformation which Portevin and Garvin found to produce a mixture of troostite and martensite: (1) that the troostite was produced as martensite at the higher transformation temperature and was drawn during the subsequent cooling to troostite, and that the martensite was the result of the lower temperature transformation directly from austenite which had escaped transformation at the higher temperature; (2) that the troostite was produced directly from austenite at the higher temperature of transformation and the martensite directly from austenite at the lower temperature of transformation. The present work shows the latter to be true. The method used by the authors discloses the mode of "delayed quenching," in which pieces may be withdrawn from the furnace and permitted to cool for a period of time in the air and then cooled rapidly. It suggests many variations in this process involving halting the cooling and retaining the piece at a particular temperature for a length of time and then quenching to produce a homogeneous structure. It is not possible in sustained cooling, except at speeds equal to or faster than critical rate, to produce a homogeneous structure, because the time at any particular temperature is not sufficient to enable the complete transformation at that temperature to take place and the subsequent cooling is not rapid enough to prevent further transformation at the lower temperatures. One would suppose, however, that further transformation at lower temperatures following the establishment of, let us say, fine pearlite would be very sluggish and that the rate of cooling of the fine pearlite, within reason, may not be a factor of considerable importance.

Of course, referring to the speed of transformation, the authors establish speeds of transformation of austenite to a particular constituent. Apparently, the rate of reaction in the austenite to pearlite transformation, which occurs at a moderately high temperature, is rapid and so is that from austenite to martensite at a very low temperature. The reaction rate producing intermediate microstructures at intermediate temperatures is very slow. This satisfactorily accounts in a large measure for the split transformation which occurs at slightly subcritical rates of cooling. In connection with the question of interrupted coolings from above Ac, it may be worth while to call attention to the fact, which has been observed, that when the cooling of pieces is halted in the region of the first transformation and then reheated, to say 1200° F., but below the Ac, the product has a fairly high tensile, strength but a comparatively low elastic limit, which may be raised by subsequently drawing the piece. This suggests that interrupted coolings are dangerous, unless intelligently and carefully controlled as to rate, temperature and time.

The portion of the paper dealing with nomenclature is rather interesting. Austenite is certainly a distinct entity and so are pearlite and martensite, though in lesser degree. Troostite, as the authors point out, has distinct etching characteristics—it etches darker and faster than martensite. Sorbite is discarded, yet in some steels

there is a condition recognized by many in the industry as sorbite. In certain nickel and nickel-chromium steels, for example, there is a condition produced by oil quenching and drawing at about 1200° F., in which the steel is fibrous, has excellent physical properties and gives high notched impact values. The microstructure is quite uniform and unlike that of any of the constituents described by the authors and one commonly called sorbite. For their purposes the names used by the authors are probably adequate to describe the structure, but it would be a distinct disadvantage to abandon the name sorbite, particularly since it is not clear that such a structure may not be produced at some intermediate temperature not studied in this work.

D. Lewis, Bridgeport, Conn.—The work that Messrs. Davenport and Bain did to produce their paper must have been colossal.

There are all sorts of things I should like to discuss, but I will keep to the theoretical discussion at the end, which is perhaps most interesting. Two explanations are put forward for the lower or Ar″ point at which martensite forms. One is that a negative ferrostatic pressure is produced owing to expansion when austenite forms; the other one is that at the upper critical range the constituent separating is ferrite, and before it separates, diffusion of carbide is necessary and that takes some time and results in considerable slowing down of the reaction as the temperature falls, but that at the lower critical point there is no diffusion of the carbide and the alpha to gamma change takes place, leaving the carbide *in situ.*

Both explanations are interesting, but I feel sure neither is complete, and we have not yet found the real explanation of what is happening. I do not think that the ferrostatic pressure theory can hold very well, because it is difficult to understand why it should take effect at the particular temperature range where that change takes place. The author has suggested that it is because the martensite at that temperature is rather stiff and will not deform. But, on the other hand, the product is incompressible at higher temperature ranges, and should still produce a negative ferrostatic pressure.

I think the other explanation is much nearer the mark; that is, that the martensite change is a change from gamma to alpha in which the carbide does not diffuse. But there is one serious difficulty that I shall point out, with the hope that the authors will do more work and get nearer to the explanation.

I will refer to Fig. 6 in the paper. At temperatures above 1100° F. the authors obtained pearlite or nodular pearlite but below they obtained so-called troostite, martensite-troostite or martensite, all of which had a needlelike structure in contrast to the parallel plate structure of pearlite. In other words, at 1100° F. the type of transformation changed. Above this temperature we get parallel plates of material separating. Below this temperature we get needles, separating. As the temperature falls, these needles get more pronounced. At 400° F. they are very pronounced, and the authors call the structure martensite-troostite. At 150° F. it is pure martensite.

It seems to me that it is at 1100° F. that the change of method of transformation occurs, because it is here that you get the change in type of structure. If that is so, why do you get the acceleration of the transformation at 300° F. instead of just below 1100° F.? It is for that reason I do not think that the explanation given by the authors is the whole story, and I feel that if somebody could explain that change of structure, we would be a little nearer the required answer.

A. V. deForest, Bridgeport, Conn.—I want to add emphatic words of praise for this paper because I know from experience how much it means to everybody who has worked in this field. It is the key that opens the door to an infinitely more accurate knowledge of what we are doing when we are heat-treating steel. I only hope that the authors will continue from this brilliant beginning and walk into the room that is now lighted up but still bare, and tell us something of the physical properties, in

other words, the practical aspects that follow this illumination. From what glimpses we have had of the physical properties as interpreted in this light, it seems as though there would be an enormous advantage to be taken from some of the mechanisms involved in this delayed quenching affair.

Honda pointed out, I believe, that a delayed quench, in the sense of a slowly formed martensitic structure, had an enormously increased impact value compared with a martensite of exactly the same hardness which was formed more rapidly. In attempting to make use of that reaction, we have studied some of this type of quenching on wire. The practical man was quenching his wire in molten lead long before delayed transformation was even suspected.

H. Scott, East Pittsburgh, Pa. (written discussion).—The authors of this paper have had the rare privilege of examining structures in steel which are entirely novel as regards the method by which they are developed. They describe their microstructures in terms of the structural units normally found after continuous quenching or tempering after such quenching. This raises the question as to whether or not all their structures are equivalent to those obtained in the conventional manner. Unfortunately, the authors do not identify their photomicrographs in terms of the heat treatment represented nor give photomicrographs of samples quenched and tempered to the same hardness in the conventional manner, information which might assist in clearing up the question stated.

With further regard to the microstructural aspects of this paper, the authors are to be commended for making an effort to define clearly the major microconstituents of hardened steel. I refer in particular to their recognition of what may now be considered a fact; namely, that "nodular troostite" is actually pearlite in a very fine state of division. This restricts the use of the term troostite to the description of structures obtained only on tempering or perhaps to quenching as they have carried it out. Regarding the martensite decomposition structures, they are explicit only as far as visual features are concerned. This situation, however, cannot be avoided unless those microconstituents are defined ultimately in terms of the physical properties of the metal, as it is entirely feasible to do, but which has not as yet been attempted. Regarding sorbite, they are justified in omitting this constituent from their list, but hardly to omit this term for the description of a product of tempering. It would be interesting to know whether or not the authors intend to imply that.

The charts showing the time required for completion of the transformation of austenite into the end products noted are of great interest. The authors apparently have not been quite successful in orienting their findings with the previously known phenomena of quenching. That is not surprising, in view of the complexity of the reactions, nor is it likely to be achieved until more experimental data are available. It may help, however, to analyze their findings from a rather different viewpoint than theirs.

When steel cools slowly at a constant rate from above the critical range, pearlite forms in a well understood manner. If the cooling is rapid and is suddenly interrupted, as in the authors' experiments at temperatures above about 500° C. in the case of steel B, the end product is the same and consequently the mechanism of its formation is the same as on slow cooling at a constant rate. The reaction occurring after interruption of rapid cooling at a low temperature, say under 100° C., is equally well understood though of quite a different nature. In this case the carbide is held in solid solution in the austenite matrix throughout the whole range of rapid cooling. Consequently the transformation Ar_3, identified under these conditions by Ar'', is lowered more or less in proportion to the amount of carbon in solid solution and in just the same way as it had been lowered by an equivalent amount of nickel or manga-

nese. The end product is martensite, which presumably contains as formed the same amount of carbon in solid solution as did the austenite from which it originated. Precipitation of carbide from the martensite starts and proceeds to the same degree as if formed near room temperatures and reheated for an equivalent temperature-time. Thus the phenomena occurring at either end of the temperature scale involved are simple at least in the sense that they are familiar.

Evidently there is a transition with diminishing holding temperature from the high-temperature or eutectic type of transformation, Ar', to the lower temperature or solid solution type, Ar''. The nature of this transition is of great interest. Is it discontinuous, as when the rate of cooling alone is varied? Apparently it is, for the authors indicate a change in structure from the fine pearlite to troostite with a hardness difference of only one point Rockwell. Does this position on their chart, Fig. 7, between 550° and 600° C. represent the temperature at which the mechanism of transformation changes from the eutectic to the solid solution type or does it simply represent the limit of resolving power of their microscope? I doubt that this point can be definitely settled, however, without other physical tests than hardness, of which resistivity and density are particularly appropriate.

At holding temperatures below 400° C., the reactions are·certainly of the solid solution type, but are somewhat more complicated than those occurring near atmospheric temperature. Nevertheless it is possible to give a simple description of what happens. Here after rapid cooling is stopped, precipitation of carbide from the austenite matrix starts and continues until the concentration of dissolved carbon in the matrix diminishes to the value at which Ar'' starts at that temperature under continuous cooling. Afterwards the reaction goes on as stated for temperatures below 100° C., steel B.

According to this view of the phenomena, precipitation of carbide from austenite controls the start of Ar'' in the temperature range 400° to 250° approximately. The lower the holding temperature in this range, the slower the rate of carbide precipitation and consequently the longer the time before Ar'' starts. This corresponds with Fig. 5 of the paper, but is not the whole story because the degree of carbide precipitation necessary to start Ar'' is smaller the lower the temperature. Of the two opposing factors, the rate of carbide precipitation is evidently the dominating one, because the time required for the start of Ar'' increases with diminishing holding temperature.

The foregoing description of the reactions with time at constant quenching-bath temperatures no longer alone accounts for those observed when the bath temperatures are below the temperature at which Ar'' starts during continuous quenching in a steel of given composition and quenching temperature. Then Ar'' starts just as it does on continuous quenching, but from the expansion data of Fig. 5, it does not go to completion until a considerable time, during which no apparent reaction occurs, has elapsed. Thus there are two stages in the progress of Ar'' in the temperature range 225° to 150° C. or thereabouts. The second stage is undoubtedly a continuation of the type of reaction observed at higher temperatures where precipitation of carbide from the austenite matrix is the controlling factor. One might expect these two reactions to go on concurrently and overlap so as to be indistinguishable. That they do not indicates that some factor other than those already considered is operating here to restrain Ar''.

The missing factor is the same as that which controls the transformation of residual austenite on tempering high-carbon steels after a normal quench, a reaction that is essentially the same as that with which we are now concerned. This factor is, the writer believes, pressure created by the expansion accompanying Ar'' after a continuous network of martensite is formed. The argument supporting this view is

given in a previous paper.[13] If pressure is the controlling factor then tempering of the martensite network is the key that releases the pressure and allows Ar″ to start again in the second stage. As the pressure development would also stop Ar″ in the first stage of the reaction, we have an explanation of the two stages shown clearly by the authors' expansion curves.

Summarizing this discussion of rapid cooling arrested at temperatures ranging from the critical point to atmospheric, the products pearlite and martensite are formed in their respective ranges of holding temperatures just as on continuous cooling. Between these extremes is a temperature range in which carbide precipitation from the austenite matrix at constant temperature controls the start of Ar″. The product of this change is troostite, which may or may not be identical in physical properties with that produced in the conventional way. There is a transition zone between this reaction and that producing martensite, in which both types occur in a manner entirely consistent with the normal reactions of tempering. The nature of the transition zone between the intermediate reaction and that producing pearlite is, however, not clear. These reactions may or may not overlap; the evidence available is insufficient to determine which is the case. Here also the factor that determines which type of reaction shall occur, that is Ar′ or Ar″, is not evident. It may be the rate of migration of carbon in austenite or again the temperature at which Ar″ starts with minimum carbon in saturated solid solution. Any further information the authors may have which bears on these evasive points will be of great interest.

Finally, the authors' experimental technique is worthy of comment. Their expansion measurements are certainly open to the criticism that they are not precise, but to the writer's mind such criticism is academic. He has accepted their data as reasonably representative of what would be obtained under ideal conditions because they have shown a well-balanced sense of values in choosing their experimental conditions. Such experimental data might be properly classified as semiquantitative, and though less desirable than purely quantitative work, it is much to be preferred over the qualitative work in this field with which the literature has been so overburdened in the past. They are to be congratulated on the skilful execution of a well-conceived investigation.

S. L. Hoyt, Schenectady, N. Y. (written discussion).—Messrs. Davenport and Bain are to be congratulated on both the conception and execution of an extremely interesting research on the transformation of austenite. Much new information is offered and new means of correlating old data are made possible. In particular, the authors have dealt with the rates at which austenite transforms into ferrite plus cementite at high temperatures and into martensite at low temperatures. In so far as I know, this is the first time that has been attempted and adds much valuable information to the small amount available on reaction velocities in metallic systems. The authors might well attempt an analysis of their results in the light of previous work on chemical systems, if for no other purpose than to set up a simple example of such a reaction.

The information given in the paper is probably not complete enough to enable others to do this but we may at least draw the outlines of such a problem. Down to about 250° C. the steel B shows the characteristics of a system changing from a metastable to a stable system and by the process of nucleation and subsequent growth. The inverse curve of that given by the authors in Fig. 7, showing the time at which the transformation begins, would give the nuclei number curve. It is obvious that nucleation is controlling over this temperature range, and that the reaction products are ferrite and cementite. This transformation can be compared to the solidification of a eutectic, the chief difference being the relatively large degree of super-cooling

[13] H. Scott: Dimensional Changes Accompanying the Phenomena of Tempering and Aging Tool Steels. Amer. Soc. for Steel Treat. (1926) 9, 277.

secured with austenite. While the authors give but few details of their method of determining the relative amounts of the phases present, it is to be presumed that their microscopical method gave correct estimates of the volume or weight percentages of austenite at different times and at the different temperatures.

The next simple reaction seems to be the one at or just above room temperature. Here the incubation period is absent and we may assume that nucleation does not control this transformation. It is not necessary for atoms of the new phase to arrange themselves in nuclei formation. Rather, a simple structural change occurs, possibly the *einfache schiebung* which was recently suggested by Scheil, which results in martensite or in a change into body-centered iron. Unfortunately for the purposes mentioned above, temperature has the reverse effect here as compared to its effect on chemical reactions, for the velocity of this change is shown to increase with decrease in temperature. At temperatures intermediate between these two, a more complex change occurs. The beginning of the transformation over the range from 160° to 250° C. for steel B is probably also due to the change to martensite, for this is suggested by both the structure observed with its martensitic markings and also by the times at which the transformations begin which fall on a smooth curve with those times for the temperatures below 160° C. Subsequent events greatly affect the course of the transformations and this may be nucleation in the martensite. This is suggested by the horizontal portions (incubation periods) of the curves for 160° and 180° C. in Fig. 5 followed by a rise later on.

A word of caution is called for by the use the authors make of length measurements as measurements of the amounts of the reacting phases. In metallic systems this particular point has always been a stumbling block to theoretical considerations. Over the higher temperatures the authors have arrived at a happy solution but I believe they should justify this use of length measurements over the lower ranges. Some time ago I attempted to make just that use of the shrinkage measurements of C. F. Brush which involved the change of martensite at room temperature, and the one positive point evolved was that the rate of change in length was not a measure of the reaction velocity. This was briefly dealt with in the Transactions of the American Society for Steel Treating,[14] while the whole paper in which this reference occurs deals with the anomalous relationships that exist between length and volume changes which militate against this use of length changes. I realize that the authors have taken the precaution of comparing the results of their two methods over intermediate temperatures but I do not believe that is sufficient. Aside from mentioning this point I do not wish to labor it, for with the objects of the present paper in mind, the authors would probably consider it of secondary importance.

I was interested in the authors' suggestion that negative pressures assist the formation of martensite. This must certainly be true when the conditions are correct, but it has been my understanding that the first martensite to form does so in spite of compressive stresses. During the quench the outer layers are under tension and the inside is under compression, at about the time martensite begins to form. This is because the outside is fairly rigid while the inside is shrinking. I believe that negative hydrostatic pressures account for deep hardening but that martensite forms on the outside in spite of compression, somewhat as outlined on pages 515 and 516 of the paper cited above.

G. M. ROBERTSON, London, England (written discussion).—It has long been known that the essential factor in the hardening of steel is the maximum rate at which austenite can decompose in the range of temperature between 500° and 600° C.

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[14] S. L. Hoyt: Stresses in Quenched and Tempered Steel. *Trans.* Amer. Soc. for Steel Treat. (1927) **11.** 522.

(930° to 1100° F). It is this maximum rate of decomposition that determines the critical rate of cooling necessary for hardening. Some very laborious investigations have been carried out in order to ascertain empirically the relations between mass, content of alloying elements, and rate of cooling, in determining hardening; but the present paper suggests a more conclusive and more scientific method of attaining this end. Alloying elements enable steel to be hardened with slower cooling and throughout larger masses because they reduce the maximum rate of decomposition of austenite. If, therefore, this maximum rate was determined for steels containing different amounts and different combinations of alloying elements, a quantitative estimate of the effect of these elements would be obtained. Each alloying element could then be given a factor expressing its relative effect on the maximum rate of decomposition, and this factor would represent the effect of the element on the rate of cooling required for hardening, and on the depth to which hardness would penetrate.

In one respect, the results obtained by the authors do not agree with existing data, and would be difficult to fit into any general theory of hardening that tried to account for certain other phenomena exhibited by steel. The results appear to show that at temperatures below 150° C. (300° F.), the decomposition of austenite proceeds with great rapidity at constant temperature, and the authors have accepted this as a fact. There is no doubt that the transition from austenite to martensite must be capable of taking place with great rapidity, for in unalloyed steels with less than 1 per cent. of carbon it cannot be appreciably prevented, even when the smallest specimens are cooled at the most rapid rates available. This only shows, however, that the transition takes place with great rapidity during continuous cooling, and does not necessarily imply that there is a range of temperature in which the austenite-martensite transition can take place with great rapidity at constant temperature. If, as the authors suggest, the austenite-martensite change was very rapid at constant temperatures below 150° C. (300° F.), then surely austenite retained by quenching would transform rapidly on tempering in this range. This, however, does not occur, and the tempering of austenite at low temperatures is actually very slow. To reconcile the facts of quenching with those of tempering, it is necessary to conclude that at temperatures below 300° C. (570° F.) there is a pronounced difference between continuous cooling and constant temperature. In support of this the following examples may be cited.

Matsushita[15] cooled specimens in water until the Ar'' change began. He then withdrew them from the water and held them in air for varying times, and finally cooled them to ordinary temperature in water. He found that the decomposition of the austenite proceeded rapidly while the specimen was cooling in water, that it practically stopped when the specimen was held in air, and that it again proceeded rapidly when the specimen was replaced in the water. He further found that if the final cooling was performed in oil instead of water, the time required to complete the change was proportional to the rate of cooling.

Tammann and Scheil[16] observed a similar phenomenon when austenite retained at room temperature by quenching was cooled to lower temperatures. In other words, they found that the austenite decomposed as the temperature was lowered, and ceased to decompose when the temperature was held constant. In fact, when austenite is retained in association with martensite at ordinary temperature, it remains undecomposed because the temperature has ceased to fall, and because its decomposition is infi-

[15] T. Matsushita: Some Investigation on the Quenching of Carbon Steels. *Sci. Repts.* Tohoku Imperial University [1], (1923–24) **12**, 7.

[16] G. Tammann and E. Scheil: Die Umwandlungen des Austenits und Martensits in gehärteten Stählen. *Ztsch. f. anorg. Chem.* (1926) **157–158**, 1.

nitely slow at constant room temperature. When, however, the steel is cooled below ordinary temperature, the transformation proceeds rapidly as the temperature falls.

Andrew, Fisher and Robertson[17] have also shown that austenite decomposes rapidly during cooling and slowly at constant temperature, and similar conclusions may be drawn from the work of Lewis.[18]

All these results go to show that the decomposition of austenite at constant temperature is a function of time; the lower the temperature, the slower the decomposition. During continuous cooling, however, the decomposition is a function of the cooling; it proceeds as the temperature falls and at a rate that depends on the rate at which the temperature falls.

The temperature range in which austenite decomposes rapidly during continuous cooling is the range in which it can transform to a solid solution of carbon in α iron; that is, the range below 300° C. (570° F.). If the austenite is quenched in any media held at a temperature below this range, the decomposition takes place before the temperature of the media is reached. The remarkable increase in the rate of decomposition of austenite observed by the authors at temperatures below 150° C. (300° F.) is therefore not attributable to an increase in the rate of decomposition at these temperatures, but to the fact that the change takes place during the few seconds required for the specimen to reach the temperature of the bath. When this temperature is attained, the change stops or proceeds very slowly at a rate that depends on the temperature. When the specimen is removed from the media, the decomposition again proceeds rapidly during cooling to room temperature. Acceptance of this view does not detract from the value of the results obtained by the authors, but it brings their results into line with existing data. The theory of the phenomena described has been outlined by Fisher and Robertson[19] and is fully described in my paper on The Effect of the Rate of Cooling on the Structure and Constitution of Steel.[20]

E. S. DAVENPORT and E. C. BAIN (written discussion).—We wish to express our thanks to all who so generously contributed to the discussion. Many have aptly elaborated our own ideas on some of the points treated only briefly in the printed paper, while others have made valuable suggestions for future work along these lines.

In the interest of brevity, we will attempt to answer most of the points raised in the discussion by presenting in some detail our own ideas of what takes place when steel is quenched. Any points that do not seem to have been covered in this manner will then be taken up separately.

Extending somewhat the views expressed in the paper we vision the mechanism of the transformation as follows:

TRANSFORMATION IN THE RANGE FROM THE EUTECTOID TEMPERATURE DOWN TO AR'

In this temperature range the transformation proceeds by rhythmic, alternate rejection of carbide and ferrite from the austenite of approximate eutectoid composition. The time required varies from infinity at the eutectoid temperature down to a very short time in carbon steel at the Ar' zone, in strict accord with chemical reactions in general, in which a stable form is developed from a metastable one. Alloy steels

[17] J. H. Andrew, M. S. Fisher and J. M. Robertson: Some Physical Properties of Steel and Their Determination. *Proc.* Royal Society (1926) **A 110**, 391.

[18] D. Lewis: The Transformation of Austenite into Martensite in a 0.8 Per Cent. Carbon Steel. *Jnl.* Iron and Steel Inst. (1929) **119**, 427.

[19] M. S. Fisher and J. M. Robertson: Discussion on (4).

[20] J. M. Robertson: Great Britain Scientific & Industrial Research Dept. *Safety in Mines Research Board Paper* 61. H. M. Stationery Office, London, 1930.

are hardenable by water quench, oil quench or air cooling, depending wholly upon the time required for transformation at the temperature of most rapid action; *i.e.*, Ar'. The product of transformation at these temperatures is pearlite of a coarseness depending upon temperature; the pearlite later spheroidizes if maintained at constant temperature. The transformation in this range of highest temperatures is comparatively simple.

Transformation in the Range from Ar' Down to About Ar''

In this temperature range the transformation time increases steadily with reduction of temperature of transformation, which is also in accord with the generally observed speeds of chemical reaction in the cases wherein atomic mobility plays an important role, superimposed upon the effect of remoteness of temperature from that of equilibrium between the two phases involved. The product of transformation in this range is distinctly different from that in the higher temperature range described above. The lamellar type of ferrite-cementite association does not appear to exist; instead there is reason to believe that the austenite transforms at least momentarily to ferrite, from which the carbide then immediately tends to precipitate. The reason for this surmise is that acicular markings, faint in the highest temperature products within the range and most distinct in the lower temperatures, are always microscopically visible. Probably the carbide rejection is almost simultaneous with the allotropic change at the elevated temperatures, but may lag far behind at the lowest temperatures in this range. The intermediate cases in the temperatures between those forming typical fine nodular pearlite and those forming recognizable, acicular troostite are very interesting and substantiate this view, for one frequently observes both types of structure associated in the same specimen. We infer that the nature of the structure is due wholly to relative rates of allotropic transformation (*einfache schiebung* referred to by Dr. Hoyt) and carbon migration or diffusion, and not directly dependant upon the time *per se*. This brief outline of the explanation most acceptable to us, at least at the present, relates particularly to the very apt criticism of Mr. Lewis, whose suggestions have been most valuable to us in reviewing our observations.

We would especially commend the use of Mr. Scott's terms "eutectic or Ar' type" of transformation and the "solid solution or Ar'' type" for what we have spoken of as "pearlitic" and "acicular" type. In this discussion we have continued our nomenclature only to avoid confusion, but the foregoing paragraphs are intended to reply to a portion of Mr. Scott's most important discussion. Our own present opinion, admittedly not necessarily our final one, does not favor his suggestion that carbide precipitates first from the austenite, although a low-carbon austenite would inaugurate Ar' at a higher temperature than an austenite of full eutectoid carbon content, a indicated in the charts of low-carbon steels.

Transformation at Ar''

The transformation of austenite at these low temperatures appears to be practically instantaneous. Carbide precipitation is almost perfectly inhibited and the martensite seems to form by the propagation of an eruptive wave through the austenite grains. This wave, if the expression may be permitted, is merely the slight shifting of atoms in the 111 atomic plane of austenite to form the 110 plane of less perfectly crystallized ferrite with carbon still atomically dispersed in a concentration far in excess of saturation. So far as our speculation has gone, there is no very clear explanation for the extraordinary circumstance of a transformation proceeding in a most leisurely fashion at about 300° F. (150° C.) suddenly completing itself in a few seconds at a temperature only 100° F. (55° C.) lower! We are therefore especially grateful for the explanation offered by Dr. Robertson and for the suggestion of Mr. Lewis, which shed light upon

this phase of the problem. In the absence of more satisfactory explanations we have mentioned the "negative ferrostatic pressure" but certainly do not feel justified in defending that idea very vigorously. The only objection we have to the Robertson theory of the transformation requiring a *falling* temperature for its procedure is found in our specimens which had appeared to reach a zero rate of change after a few minutes at a *constant* temperature of about 285° F. (140° C.). No further transformation, as evidenced by expansion data, was observed when such specimens were subsequently cooled to 70° F. (20° C.). Evidently the transformation had completed itself at *constant* temperature in a few minutes at 285° F. (140° C.) since no austenite remained to transform upon further rapid cooling.

Referring now to some other specific points brought out in the discussion. We would not wish to be misunderstood as suggesting any significant changes in nomenclature. Indeed, we have only omitted the word "sorbite" in discussing the structures found in our various series for the reasons indicated, and certainly have no doubts at all as to its having the most definite sort of meaning as applied to tempered structures. Possibly some of the structures designated as troostite, if retained at the bath temperature for extended periods of time, would have changed by carbide coalescence to a product to which the name "sorbite" would apply appropriately.

The microstructures of similarly treated specimens from the various steels investigated resemble one another sufficiently to warrant the expedient of printing only representative photomicrographs. Figs. 15 to 20 inclusive are of steel A; Figs. 15 and 16 are from the 1275° F. (691° C.) bath temperature; Figs. 17 and 18 are from the 1200° F. (694° C.) bath temperature; Figs. 19 and 20 are from the 800° F. (427° C.) temperature. Figs. 21 and 22 are of steel F as transformed respectively at 284° F. (140° C.) and at 527° F. (275° C.).

At the present time we are engaged in establishing the fundamental difference between steels transformed at elevated temperatures and steels which first transformed to martensite and subsequently were tempered, or drawn back, to comparable physical properties. In our experience the microscopic appearance is quite different when corresponding temperatures are employed.

The expansion measurements employed to follow the progress of the reaction are unquestionably not adequate, as pointed out by Dr. Hoyt. We are of the opinion, however, that the end of the transformation is fairly well marked by the end of the expansion period. Accordingly we have not drawn any conclusions involving the rates of reaction in the lower temperature ranges.

Progress Notes on the Iron-silicon Equilibrium Diagram

By Bradley Stoughton* and Earl S. Greiner,† Bethlehem, Pa.

As a part of the systematic study of the alloys of iron under the auspices of the Engineering Foundation, and preliminary to the commencement of comprehensive work on this larger subject, the authors have undertaken an investigation of the available literature dealing with the alloys of iron and silicon. The purpose is to collect all the data in English and foreign languages and present them in two monographs, one of a more scientific and the second of a more industrially useful nature. Of course, a great deal of information upon the constitution of the iron-silicon alloys was found specifically upon the changes of phase in the equilibrium diagram and the different phases present, such as solid solution, chemical compounds (iron silicides), etc. While no extended research was contemplated in the particular study undertaken, nevertheless the data collected proved to be so contradictory in many respects that a simple study of some of the outstanding problems involved in the constitution and equilibrium diagram was undertaken. Because research was not a primary object of the work, and also because of the extreme industrial importance of the silicon alloys between 0.80 and 14 per cent. silicon, and finally because of the unsatisfactory state of knowledge existing as to these alloys, the experimental investigation was limited entirely to alloys with less than 10 per cent. silicon.

Discussion of Continuous Series

It has often been said in print that the iron-silicon alloys form a continuous series of solid solutions from 0 to 15 per cent. silicon. This claim the authors are inclined to doubt: first, because the alloys from 0 to 4.25 per cent. silicon are ductile and malleable at atmospheric temperature, while those with 5 per cent. or more of silicon are comparatively hard and brittle. Furthermore, the alloys with more than 4.25 per cent. silicon are comparatively hard and low in ductility at atmospheric temperature, but become much more ductile when heated slightly. It is well known, for example, that the alloy containing 4.75

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† H. M. Byllesby Fellow, Lehigh University, and Fellow of the Engineering Foundation.
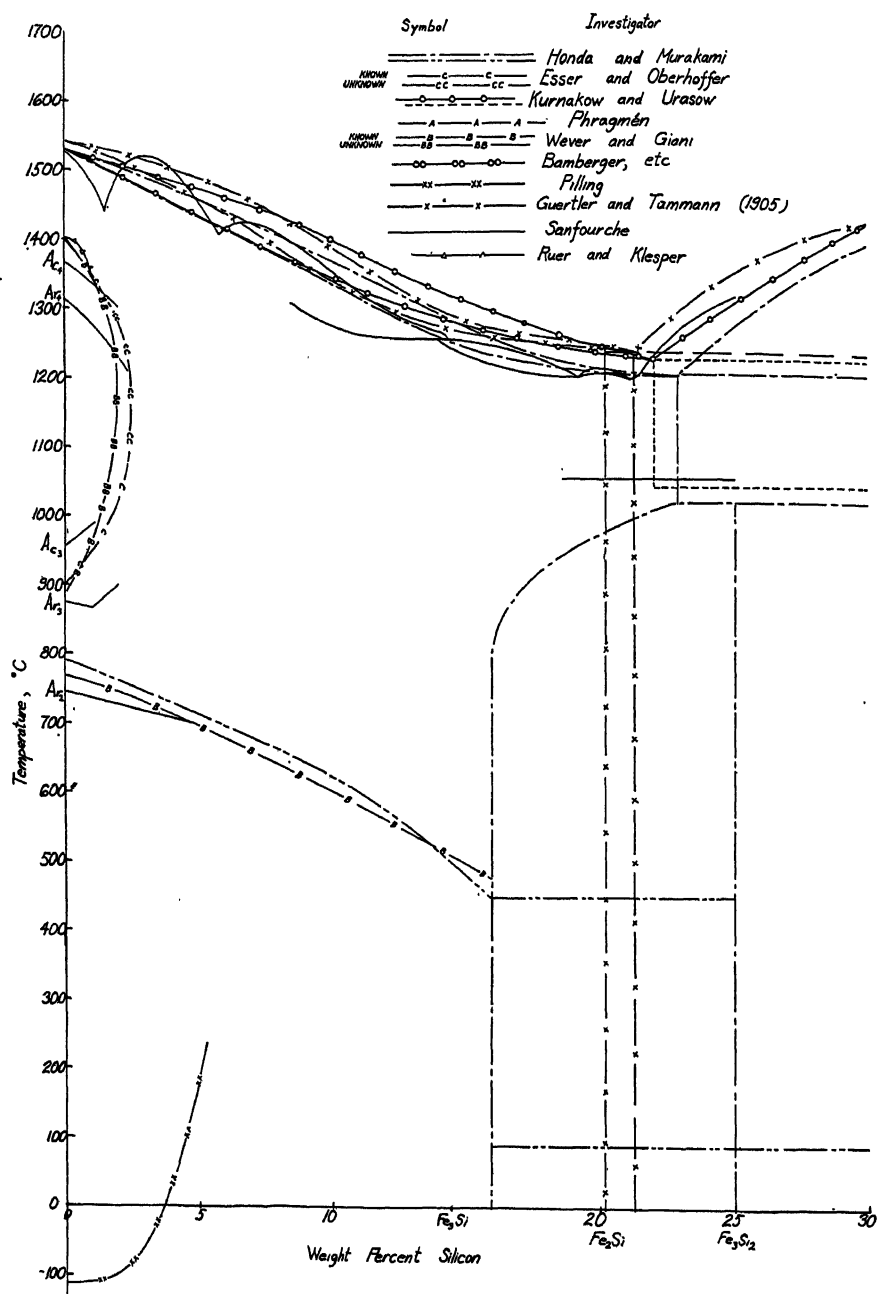
FIG. 1a.

FIG. 1.—SUMMARY OF OBSERVATIONS OF CHANGE POINTS IN FE-SI SERIES.
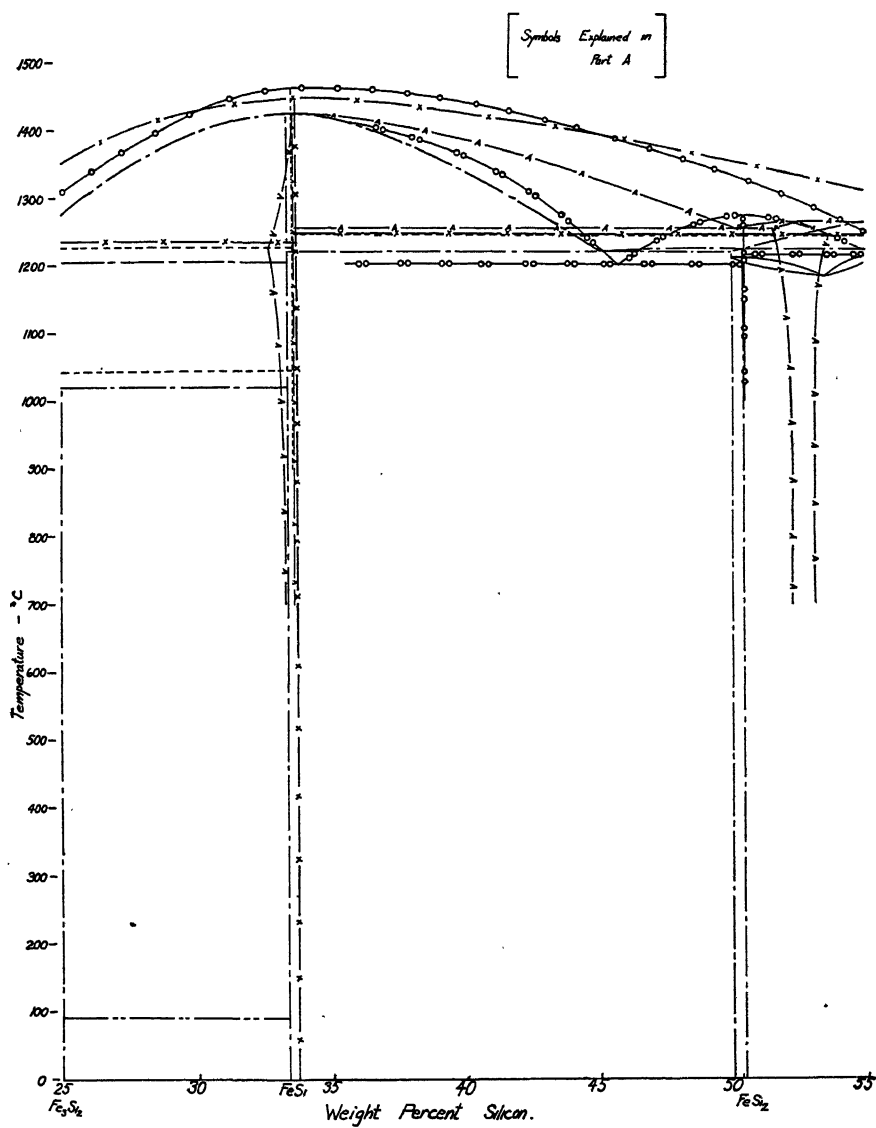
FIG. 1b

per cent. silicon will crack when sheared cold, whereas it will give a good edge if sheared in boiling water.[1,2]
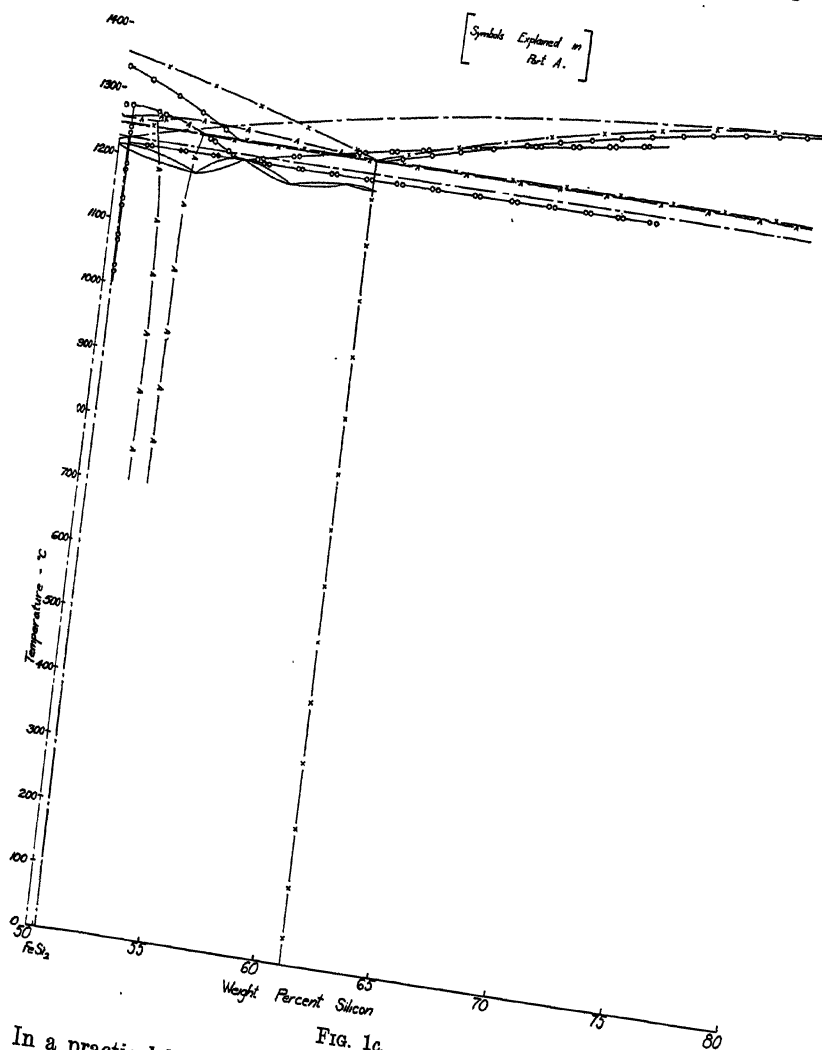
FIG. 1c.

In a practical but significant study of the alloys up to 5 per cent. silicon, Pilling drew a line representing approximately the limit between

[1] N. B. Pilling: Low Temperature Brittleness in Silicon Steels. *Trans.* A. I. M. E. (1923) **69**, 780.

[2] A. Pomp: Einfluss des Siliziums auf die Festigkeitseigenschaften des Flusseisens bei erhöhter Temperatur. *Mitt.* Kaiser Wilhelm Inst. für Eisenforschung. (1925) **7**, 105–112.

ductile and comparatively nonductile low-silicon alloys at different temperatures from $-100°$ to $+200°$ C. This line is shown in the lower left-hand corner of Fig. 1a. Pilling's work is sufficiently convincing to
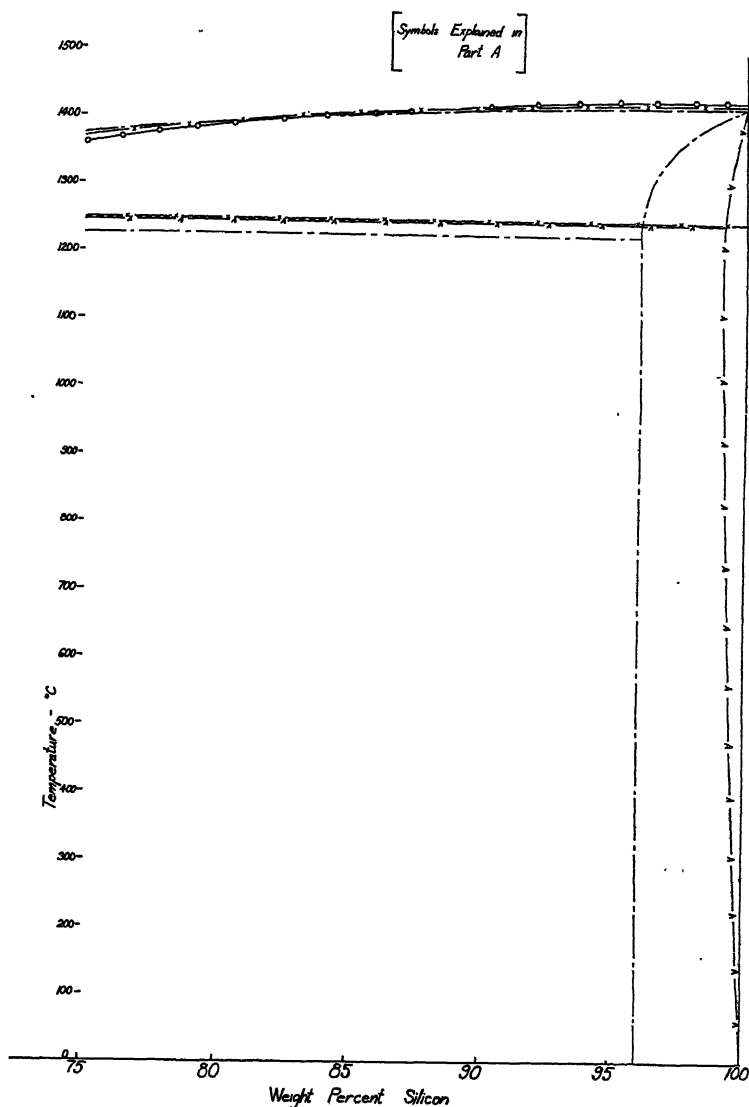
FIG. 1d.

disprove the existence of a continuous series of solid solutions from 0 to 6 per cent. silicon. Furthermore, the almost (if not quite) universal ductility that is characteristic of iron-rich solid solutions would also indicate that the alloys above 4.25 per cent. silicon are not solid solutions

at atmospheric temperature. The authors' experimental investigations were addressed, therefore, to a study of possible changes of phase in alloys below 10 per cent. silicon and at temperatures corresponding to the abrupt changes in ductility located by Pilling. The many investigators who have previously studied the iron-silicon-equilibrium diagram did not discover any changes of phase in this portion of the diagram, but the present authors believe that this evidence is not conclusive, because, first, any change points existing at these temperatures and concentration are extremely difficult to find, even though the investigators use approved methods of locating arrests and also special methods, such as magnetic means, X-ray spectrometer, etc. Moreover, the
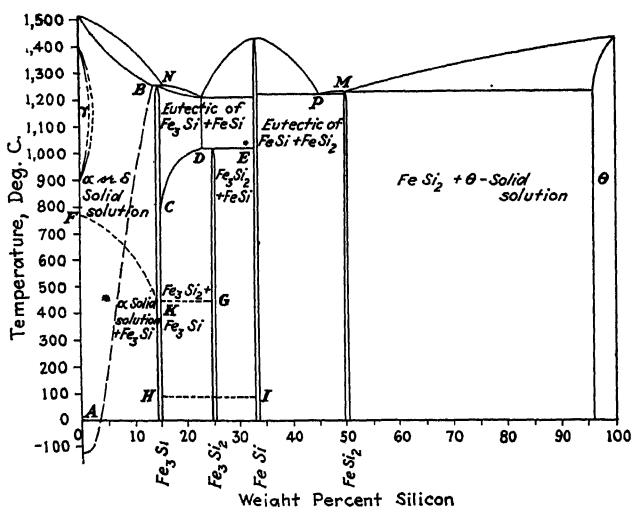
FIG. 2.—TENTATIVE IRON-SILICON EQUILIBRIUM DIAGRAM.

changes, if they did exist, would represent extremely small variations in phase, which would give only slight indications. And, furthermore, as one of the investigators pointed out,[3] "the transformations take place seemingly through a very extended range and go too slowly to be recorded." Another reason why changes of phase here, if they exist, might have been overlooked is the circumstance that some of the investigators discontinued recording observations after cooling below about 400° to 500° C.

In Fig. 1 is given a summary of the observations so far made on change points in the series, from which it will be seen that there is considerable disagreement between the several investigators in some essential features. These differences are due, no doubt, in some cases to impurities in the alloys used. The early investigators especially did not have available alloys that were sufficiently free from carbon to be unaffected.

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[3] M. G. Corson: Private communication, Oct. 24, 1928.

The evidence from these change-point investigations is, however, supplemented by many researches upon the different iron silicides which exist and which we are discussing in some detail below.

From these combined investigations and from the brief study made on a few alloys below 10 per cent. silicon, the authors have constructed a tentative diagram (Fig. 2). The most important part of this diagram from the industrial standpoint is the lower left-hand corner, because the rolling, shearing, punching and annealing of so-called transformer sheets containing, for optimum results, 4.75 per cent. silicon and the smallest possible amount of other ingredients, is in the range which is almost, but not quite, ductile at atmospheric temperatures. In Fig. 1 are included only original observations.

PREVIOUS RESEARCH ON IRON-SILICON COMPOUNDS

Each of the following compounds has been reported by at least two competent investigators: Fe_3Si, Fe_2Si, Fe_3Si_2, $FeSi$ and $FeSi_2$. There is, however, conflicting evidence as to all but one of these; namely, $FeSi$, which we may accept from the testimony of many. The others will be discussed in detail in this paper and evidence given pro and con. The difficulties of deciding which researcher is correct are due to the varying degrees of purity of the alloys studied by each, the uncertainty of chemical analysis caused by possible presence of SiO_2 in some residues believed to be pure silicide, the elusiveness of some change points in the equilibrium diagram, and the lack of knowledge of these pitfalls which has caused some investigators to report the presence of silicides on evidence that is not entirely convincing. The presence of a well-established eutectic at about 21 per cent. Si, which is very close to the composition of the alleged silicide, Fe_2Si (20 per cent. Si), may have been misleading both as to the presence or absence of such a silicide. From the equilibrium diagram it does not seem probable that Fe_3Si. Fe_2Si and Fe_3Si_2 all have a place in normal, slowly cooled, pure iron-silicon alloys at atmospheric temperatures. After a discussion of the available evidence, the probabilities will be compared, but always with the reservation that the points cannot be settled until some research is made on pure alloys under conditions which ensure the establishment of equilibrium.

FE_3SI

Corson[4] claims that his photomicrographs (see his Figs. 31 to 40) indicate the existence of Fe_3Si. He further says that this is confirmed by X-ray analysis (pages 277–8). He also finds a marked increase in

[4] M. G. Corson: The Constitution of the Iron-silicon Alloys, Particularly in Connection with the Properties of Corrosion-resisting Alloys of This Composition. Iron and Steel Technology, A. I. M. E. (1928) 249.

electrical conductivity at 14.3 per cent. Si (page 259); and he says there is an increased resistance to corrosion, the closer the analysis approaches 14.3 per cent. silicon. His hardness curve also shows a critical point at 14.3 per cent. Si (Fig. 13, page 261).

Phragmén[5] finds a uniform space lattice at 14.5 per cent. Si and he also writes as follows:[6] "The minimum of the electric resistivity curve obtained by Corson at about 15 per cent. Si surely corresponds to the formula Fe_3Si. At this composition the distribution of the substituting Si atoms in a body-centered alpha-iron lattice will be most regular." Finally Bain[7] also found a steady decrease in the lattice parameter as the composition ranged from pure iron to 14.5 per cent. silicon and from this composition up to 20 per cent. it remains constant.

Sanfourche[8] found a peritectic change at the solidus-liquidus at 14.3 per cent. silicon. While this evidence seems somewhat scanty, it is, nevertheless, supported by some high authorities in this field. It is also flatly contradicted by another high authority, T. Murakami:[9] "The presence of the compound Fe_3Si is not concluded by the fact that the minimum point in the electric-resistivity curve corresponds to the composition of the formula, Fe_3Si. I believe that this is saturation limit in the alpha solid solution. The difference for the saturation limit (14.5 per cent. Si in his (Corson) paper and 16 per cent. Si in my result) is attributed to the difference of treatment of specimens measured; that is, in his case, sand-cast bars were used, while in my experiment well-annealed specimens were used.

"In his diagram (Fig. 10 of his paper), moreover, curves *HI* and *FI* are very doubtful. There is no experimental evidence."

Fe_2Si

Hahn[10] made a synthetic alloy by melting reduced iron under a slag and adding some silicon and sodium to it. He treated it with HCl and obtained a residue of which he made a checked analysis coming very close to Fe_2Si.

Moissan[11,12] quoted the work of Hahn and then repeated it, using pieces of soft iron and crystals of silicon. The silicon cemented the

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[5] G. Phragmén: Ueber den Aufbau der Eisen-Silizium-Legierungen. *Stahl und Eisen* (1925) **45**, 299.

[6] G. Phragmén: Private communication, Sept. 25, 1929.

[7] M. G. Corson: *Op. cit*, 295.

[8] M. A. Sanfourche: Contribution à l'Etude des Ferro-Siliciums. *Rev. de Mét., Mem.* (1919) **16**, 217.

[9] T. Murakami: Private communication, Nov. 13, 1929.

[10] Hahn: Liebig's *Annalen* (1864) **129**, 57–81

[11] H. Moissan: Etude de quelques composés du silicium. *Ann. de Chimie et de Phys.* [7] (1896) **9**, 289.

[12] H. Moissan: Action du silicium sur le fer, le chrome et l'argent. *Compt. rend.* (1895) **121**, 621–624.

iron. Moissan treated the resulting alloy with dilute HNO_3, decanted, washed, and then analyzed the residue. The analysis indicated the compound Fe_2Si.

Carnot and Goutal[13] treated ferrosilicon low in manganese with cold, very dilute H_2SO_4 for 15 days. This left a complex residue containing principally carbon, various silicides, and hydroxide of silicon. The hydroxide of silicon and the FeSi were dissolved in hot, dilute potash solution. This left hydroxides of iron and manganese, which were dissolved by dilute H_2SO_4. From the residue still left, particles were removed by a magnet. These were proved by chemical analysis to be Fe_2Si.

Lebeau[14] reviewed the work of his predecessors and then himself made a magnetic crystalline residue which proved by analysis to be Fe_2Si. He made this by melting iron with a copper-silicon alloy, treating the resulting metallic button with dilute nitric acid until the copper portion was completely dissolved. The spongy mass remaining was washed in soda, then nitric acid and water. It analyzed Fe_2Si. He then proved[15] that the compound Fe_2Si is not decomposed even when dissolved in melted silver and even when the silver was boiled in an electric furnace at a temperature of 1000° C. Finally, by dissolving FeSi in melted silver and treating the resulting button with nitric acid, he obtained a residue of Fe_2Si and SiO_2.

It is to be observed that the various residues analyzing Fe_2Si give somewhat different properties in resistance to acid, which might be held to throw doubt upon their existence as a compound. For example, Hahn found that Fe_2Si was left as a residue from HCl attack, while Lebeau dissolved it in HCl.

Carnot and Goutal say that the Fe_2Si made by Moissan in the electric furnace is not attacked by acid, whereas the Fe_2Si obtained as a residue from blast-furnace products is easily attacked by hot acids, even when dilute. Lebeau explains this difference by the fact that some Fe_2Si is surrounded by an envelope of opalescent silica which makes it immune from attack.

Murakami[16] says that thermal analysis and magnetic analysis indicate the entire absence of Fe_2Si and that photomicrographs do not indicate its presence.

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[13] A. Carnot et Goutal: Recherches sur l'état où se trouvent le silicium et le chrome dans les produits sidérurgiques. *Compt. rend.* (1898) **126**, 1240–1245.

[14] P. Lebeau: Sur le siliciure de fer Si Fe₂ et sur sa présence dans les ferrosiliciums industriels. *Compt. rend.* (1900) **131**, 583–586.

[15] P. Lebeau: Sur l'état du silicium dans les fontes et les ferrosiliciums à faible teneur. *Compt. rend.* (1901) **133**, 1008–1010.

[16] T. Murakami: On the Equilibrium Diagram of the Iron-Silicon System. *Sci. Repts.* Tôhoku Imp. Univ. (1921) **10**, 85.

Phragmén[17] says that X-ray spectrometry does not show the presence of Fe_2Si. Furthermore, Osmond,[18] Troost and Hautefeuille,[19] Le Chatelier[20] and Stead [21] have not found it.

Fe_3Si_2

De Chalmot,[22] Murakami[23] and Phragmén[24] all report the presence of Fe_3Si_2, whereas Corson[25] claims that it does not show under the microscope, or by X-ray analysis, or change point in electrical resistivity tests. In any event, it does not seem to have an important effect on the equilibrium diagram, or to have made its presence felt in any of the liquidus-solidus curves. Murakami[26] gives very strong evidence of a peritectoid reaction at 1020° C., on cooling and says that thereby Fe_3Si_2 is formed in all the alloys containing from 23 to 33.3 per cent. of Si. This observation is repeated in the monograph of Honda and Murakami[27] three years later. This compound was first doubted by Phragmén[28], but he later asserted that his 1923 specimens were not sufficiently annealed, and that he finds Fe_3Si_2 by X-ray analysis.[29] The chief difference regarding the presence of this compound seems to be due to the necessity for an anneal of more than 30 min. at 1000° C. and a sufficient etching with any acid[30] in order that it may be seen under the microscope or by X-ray analysis. Of course, if it formed by a peritectoid reaction from FeSi, as reported by Murakami, its presence would not be indicated in the solidus-liquidus curve.

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[17] G. Phragmén: The Constitution of Iron-Silicon Alloys. *Jernkontorets Ann.* (1923) **107**, 121.

[18] F. Osmond: Recherches calomstrianes sur l'état du silicium et de l'aluminum dans les fers fondus. *Compt. rend.* (1891) **113**, 474.

[19] L. Troost et P. Hautefeuille: Etude calorimétrique des siliciures de fer et de manganèse. *Compt. rend.* (1875) **81**, 264.

[20] H. Le Chatelier: Sur la résistance électrique des aciers. *Compt. rend.* (1898) **126**, 1709.

[21] J. E. Stead: The Crystalline Structure of Iron and Steel. *Jnl.* Iron and Steel Inst. (1898) **53**, 145.

[22] G. de Chalmot: On Silicides of Iron. *Jnl.* Amer. Chem. Soc. (1895) **17**, 923–924.

[23] T. Murakami: *Op. cit.*

[24] G. Phragmén: The Constitution of Iron-Silicon Alloys. *Jnl.* Iron and Steel Inst. (1926) **114**, 397.

[25] M. G. Corson: *Op. cit.*, 278 and Figs. 33 to 41 incl.

[26] T. Murakami: *Op. cit.*

[27] K. Honda and T. Murakami: On the Structural Constitution of Iron-Silicon-Carbon Alloys. *Sci. Repts.* Tohoku Imp. Univ. (1923) **12**, 14–15.

[28] G. Phragmén: See ref. 17.

[29] G. Phragmén: Ueber den Aufbau der Eisen-Silizium-Legierungen. *Stahl und Eisen* (1925) **45**, 299.

[30] T. Murakami: Private communication, Nov. 13, 1929.

Most Probable Iron-silicon Compounds

No doubt has been expressed as to the compound FeSi. The compound $FeSi_2$ rests on the work of Murakami,[31] Bamberger,[32] de Chalmot,[33] Phragmén,[34] Hengenstenberg,[35] Hahn[36] and Pick.[37]   While Phragmén[38] said that the photomicrographs left some doubts as to the presence of $FeSi_2$, it would appear to us that his X-ray evidence in reference 17 and also in reference 24 indicates a single homogeneous phase at the composition $FeSi_2$.   In any event, no denial of this compound has ever been published.   We may, therefore, tentatively accept it also.

As to the compounds Fe_3Si, Fe_2Si and Fe_3Si_2, we are somewhat doubtful that all of these exist at atmospheric temperature in normal, pure, slowly cooled iron-silicon alloys.   It is reasonably clear that, if Fe_3Si_2 is present, it is the result of a peritectoid reaction resulting from the breaking down of FeSi on cooling.   Murakami's[39] equilibrium diagram shows this peritectoid line definitely crossing the concentration of 20 per cent. Si.   If this is true, it eliminates Fe_2Si as an equilibrium phase.   Furthermore, this peritectoid line comes reasonably close to touching the concentration Fe_3Si.   That is, it is drawn to 16 per cent. Si(Fe_3Si = 14.3 per cent. Si).   The reason Murakami stopped at 16 per cent. was because his magnetic transformation shows a distinct break at that point.   (See Fig. 1.)   But in view of the work of Corson, Phragmén, Bain and Sanfourche, we believe the preponderance of evidence is in favor of the compound Fe_3Si.

Further reasons for doubting the existence of Fe_2Si are the magnetic observations of Murakami[40] which showed a change point from diamagnetic to paramagnetic alloys at temperatures decreasing from about 770° C. with 100 per cent. Fe to 450° C. with 16 per cent. Si.   The line is then horizontal at 450° C. to 27 per cent. Si.   He also finds another magnetic change point at 90° C. which is horizontal between 16 and 30 per cent. Si.   Phragmén[41] also obtains a uniform decrease of lattice parameter with increasing silicon content from 100 per cent. Fe to 15.4 per cent. silicon.   From this point on the lattice parameter is constant

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[31] K. Honda and T. Murakami: *Op. cit.*

[32] M. Bamberger, O. Einerl and J. Nussbaum: Untersuchen über technisches Ferrosilizium.   *Stahl und Eisen* (1925) **45**, 141.

[33] G. de Chalmot: *Op. cit.*

[34] G. Phragmén: See ref. 24.

[35] O. Hengstenberg: The Density of Iron-Silicon Alloys and their Relation to the Phase Diagram.   *Stahl und Eisen* (1924) **44**, 914–915.

[36] Hahn: *Op. cit.*

[37] W. Pick: Dissertation, Karlsruhe, 1906.

[38] G. Phragmén: See ref. 17.

[39] T. Murakami: *Op. cit.*, 81, Fig. 1.

[40] T. Murakami: *Op. cit.*

[41] G. Phragmén: See ref. 24.

to 25 per cent. Si. These X-ray results are checked by Bain[42] who, however, only went up to 20 per cent. Si, which is the concentration of the alleged Fe_2Si. Right up to this point, however, there is indication of no irregularity indicating a compound. Guertler and Tammann[43] published photomicrographs which they at first interpreted as exhibiting crystals of Fe_2Si. Later they abandoned this idea, in view of later research by other investigators. The only direct evidence of the existence of Fe_2Si is chemical isolation and concentration and, while this evidence is striking, it is to be noted that in every case the alloys were not pure but were modified by the presence of some such element as carbon, copper, silver, etc. For the present, therefore, the authors are not including Fe_2Si as a normal constituent.

CHANGE OF PHASE

We thought that the line traced by Pilling might represent a series of changes of phase in the equilibrium diagram. If this were so, a discontinuity in physical properties should occur when the alloys are heated and cooled so as to pass over this line of "critical ductility." For instance, the temperature coefficient of electrical resistance should undergo a discontinuity as the alloys cross this line. The several investigations of expert observers who have already worked in this field had failed to reveal any changes of phase in the alloys in this part of the diagram. Thermal, magnetic and X-ray researches had been tried without result. Therefore it was thought advisable to carry out some electrical resistance determinations on these alloys, with the object of determining if change points too slight, or too gradual, to be indicated by the other methods might not be located. This method has never been used before for locating change points in the equilibrium diagram of iron-silicon alloys. It will be noticed that the line traced by Pilling (see Fig. 3, line AB) is below atmospheric temperature in one part and very steep in another part. These conditions alone are sufficient to account for its not having been located previously as a change of phase, since investigators naturally do not normally cool below atmospheric temperature and since a line almost vertical in direction is extremely difficult to locate.

The results of the temperature-electric resistance determinations on all the alloys prepared, except the 8.57 per cent. silicon alloy, will be reported in this paper. Since it was impossible to drill holes in the 8.57 per cent. silicon alloy, the method of making the electrical connections to the silicon steel bars containing less than 8.57 per cent. silicon (method

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[42] See M. G. Corson: *Op. cit.*

[43] W. Guertler and G. Tammann: Über die Verbindungen des Eisens mit Silicium. *Ztsch. anorg. Chem.* (1905) **47**, 163.

to be described later) could not be used for the latter alloy.   The method
used for making the electrical connections to the 8.57 per cent. silicon
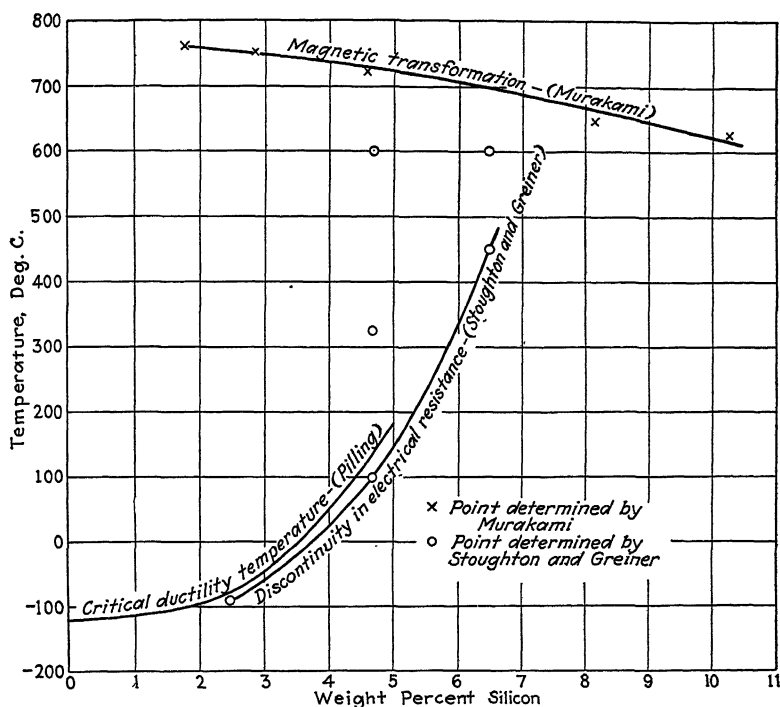
FIG. 3.—CHANGE POINTS IN IRON-SILICON ALLOYS CONTAINING LESS THAN 11 PER
CENT. SILICON.

alloy permitted excessive oxidation of the contacts.   Therefore, doubt
was thrown on the accuracy of the latter determinations, and they will
not be reported herein.

APPARATUS AND METHODS OF DETERMINATION

The apparatus used for determining the change in electrical resistance
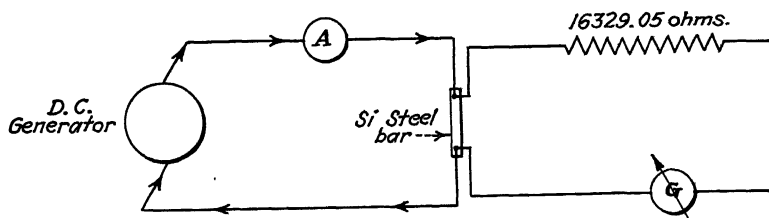
FIG. 4.—ELECTRICAL CIRCUIT USED IN RESISTIVITY MEASUREMENTS.

of the other alloys, on heating and cooling, is shown in Figs. 4 and 5.
Fig. 4 shows the electric circuit used.   The entire circuit used direct

current, which was supplied by means of a motor-generator set. By use of a heavy current (9 to 12 amp.) through the silicon-steel bar, it was possible to obtain a fairly accurate measurement of the electric resistance of the bar.

A d'Arsonval reflecting galvanometer (Fig. 5) was used to measure the voltage drop across the silicon-steel bar. The resistance of 16,329.05 ohms was inserted in series with the galvanometer, so as to prevent the reflected beam of light from the galvanometer mirror from traveling off the translucent scale. The current and galvanometer readings were taken simultaneously, and although the current fluctuated slightly, a correction factor was obtained whereby it was possible to correct all the
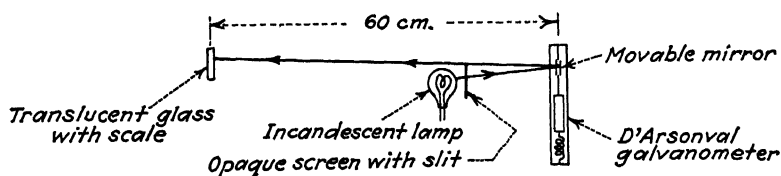
FIG. 5.—GALVANOMETER AND SCALE.

galvanometer readings of each run to a constant current. A storage battery could not be used because the current required was too high, and the length of the time required for each run was too long. The galvanometer readings are given in units, which are simply the divisions used on the translucent scale. Since the aim of this research was simply to measure the relative change of resistivity with temperature, it was possible to plot galvanometer readings against temperature (current in bar and all external resistance beside the bar remaining constant) and thereby note the effect of temperature on the electric resistance of the iron-silicon alloy in question.
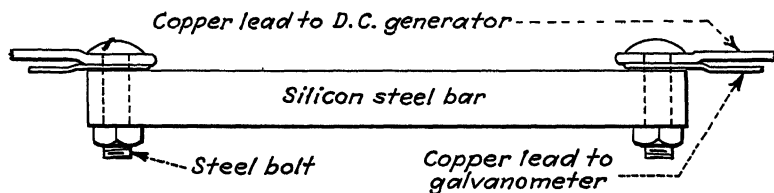
FIG. 6.—METHOD OF MAKING ELECTRICAL CONNECTIONS TO STEEL BAR.

Considerable trouble was encountered because of poor electrical contacts between the silicon-steel bar and the copper connectors. This trouble was caused by the ease with which the contacts became oxidized when the bar was heated. For a while, it was thought that a certain one of these alloys had a negative temperature-coefficient of electric resistance; until finally the cause of the latter phenomenon was found to be an oxide film between the copper connectors and the silicon-steel bar.

The method finally used to make the connections·between the copper wire and the steel bar is shown in Fig. 6. The wire which measures the voltage drop across the bar was bolted between the wire carrying the heavy current and the steel bar. The contact surfaces of both the bar and the wires were thoroughly cleaned before each run. The fact that the electric resistance of the bar was almost exactly the same before and after the runs indicates that no appreciable change in electric resistance was due to oxide on the contacts. Copper wire was used for the electrical connectors because it has no allotropic modifications at the temperatures of these determinations.

The bar with the connecting wires was then placed in a Westinghouse electric heat-treating furnace. The bar was placed parallel to the furnace door so as to insure even heating, and also to maintain an equal temperature at both connections of the bar to the copper wires, thereby avoiding thermoelectric effect. The temperatureo f the specimen was measured
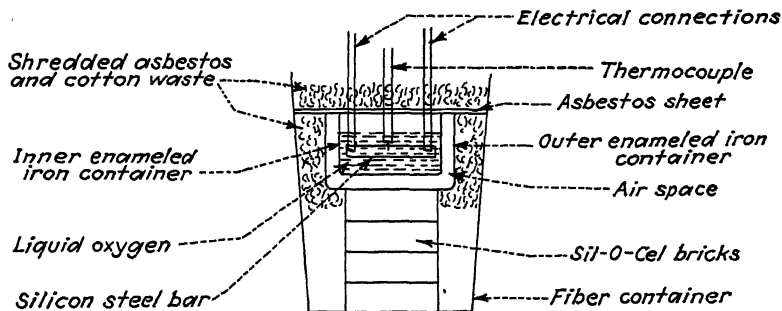
FIG. 7.—APPARATUS USED FOR TEMPERATURES BETWEEN −183° C. AND 25° C.

by placing the tip of a base-metal thermocouple at the center of the bar. For record, the current was turned on and off the furnace, and this proved to have no effect on the galvanometer readings.

The apparatus used to measure the electric resistance of the 2.44 per cent. silicon alloy from the temperature of liquid oxygen to room temperature was essentially the same as that previously described except that the copper wires were soldered to the silicon-steel bar and the bar was placed in a heat-insulating device such as shown in Fig. 7. The bar was first covered with liquid oxygen; after the oxygen had evaporated from the surface of the bar, the temperature rose but was prevented from rising too rapidly because of some remaining liquid oxygen in the bottom of the container,and also because of the heat insulation.

The alloys were made by melting 1½ kg. of electrolytic iron and silicon of 97 per cent. grade in magnesia crucibles. The heating was done in an Ajax-Northrup induction furnace and the alloys were held in the molten state for at least ½ hr. after the entire charge was melted. The stirring action of the eddy currents and the time during which the

alloys were maintained liquid insured homogeneous melts. The alloys were sand-cast into bars about $\frac{5}{8}$ in. dia. and 7 in. long. The 4.68 per cent. and the 6.48 per cent. silicon bars were given a preliminary annealing at 950° C., while the 2.44 per cent. silicon bar was tested in the cast state. Table 1 gives the silicon content of the alloys prepared:

TABLE 1.—*Silicon Content of Alloys Prepared*

No.	Silicon, Per Cent.	No.	Silicon, Per Cent.
1	2.16	4	6.34
2	2.44	5	8.57
3	4.68	6	6.48

The 4.68 per cent. silicon alloy was also tested in the temperature range between −15° C. and +176° C. The apparatus used for this test is shown in Fig. 8. The bar was mmersed in ethylene glycol and the temperature lowered to the freezing point of ethylene glycol by means of "dry ice" or solid carbon dioxide. The temperature of the ethylene glycol bath was then allowed to rise to room temperature and from that point it was heated to 176° C. by means of a Bunsen burner. The copper connections were soldered to the silicon-steel bar.
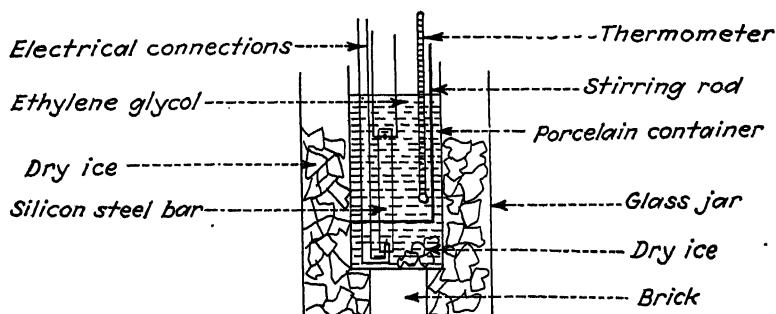
FIG. 8.—APPARATUS USED FOR TEMPERATURES BETWEEN −15° C. AND 176° C.

While the silicon-steel bars were originally 7 in. long, they were accidentally broken in some cases, either because of defects in the cast specimens or because of the excessive brittleness. The shortest bar had a length of about 4.75 inches.

DISCUSSION ON RESULTS OF ELECTRIC-RESISTANCE MEASUREMENTS

The results of the electric-resistance determinations are shown in Figs. 9 to 21. The curves for the 6.48 per cent. silicon alloy exhibit a break or point of inflection at about 450° C. on heating, as shown in runs M and Q (Figs. 9, 11) on heating, and at 400° C. and 450° C. on

cooling in runs N and R (Figs. 10, 12). Run N is the cooling curve of run M. The specimen in runs M and N was held at a temperature between 700° and 800° C. for about 10 hr. before it was permitted to cool, while in runs Q and R the specimen was held at the temperature of 700° C. for only approximately 15 min. A marked discontinuity was noted between
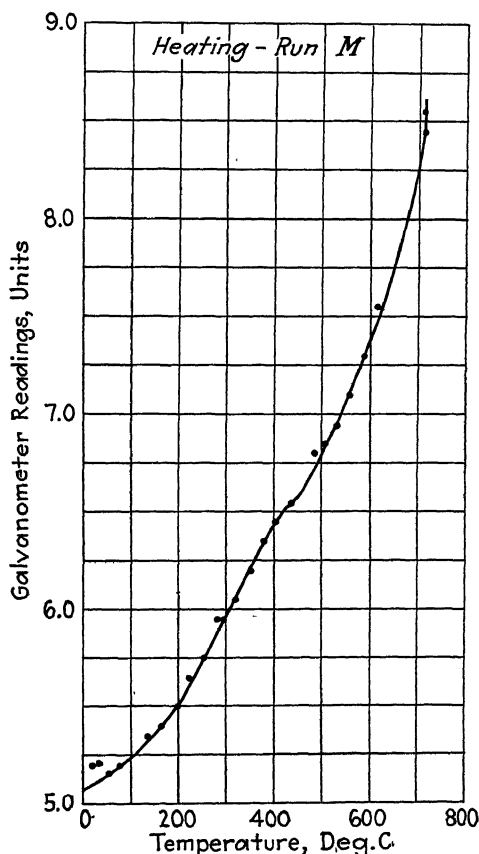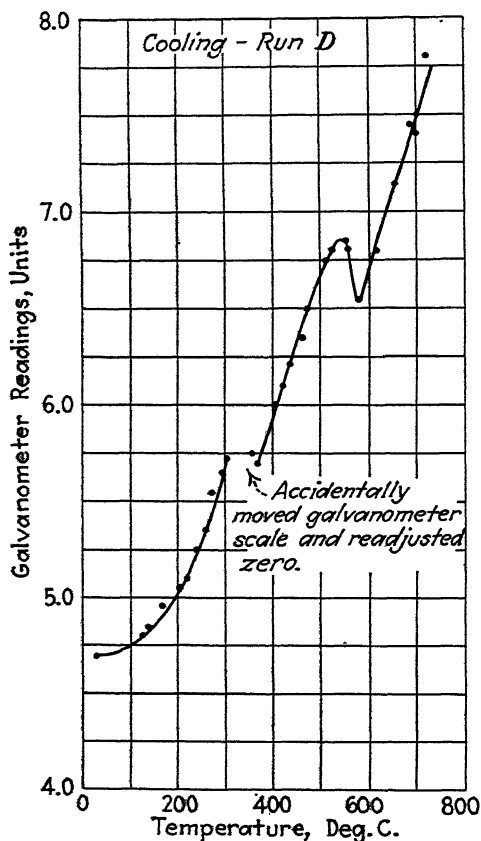
Fig. 9.—Fe-Si alloy containing 6.48 per cent. Si. Relative electric resistance at various temperatures. Galvanometer readings corrected to 7.5 amperes.

500° and 600° C. in run N. A similar discontinuity was observed in the cooling curve of run F (Fig. 15) of the 4.68 per cent. silicon alloy at the same temperature. The only thing that has ever been discovered by previous investigators, which checks roughly with this point between 500° and 600° C., is a magnetic transformation observed by Wever and Giani[44] and also by Murakami;[44] although the magnetic transformation points occur at a slightly higher temperature than the points in runs F and N. The heating curves, runs M and Q, exhibit a bend at about 200° C.

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[44] F. Wever and P. Giani (reference 49); also T. Murakami: *Op. cit.*
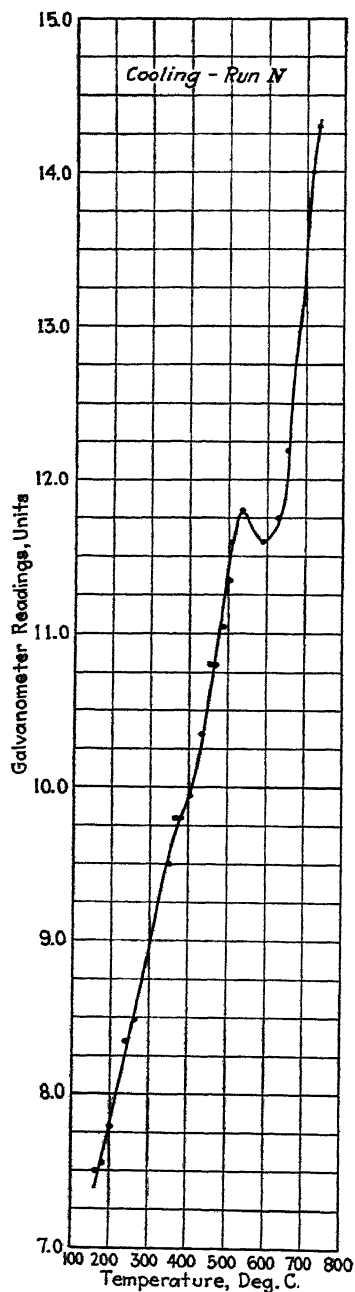
FIG. 10.—FE-SI ALLOY CONTAINING 6.48 PER CENT. SI. RELATIVE ELECTRIC RESISTANCE AT VARIOUS TEMPERATURES. GALVANOMETER READINGS CORRECTED TO 7.5 AMPERES.
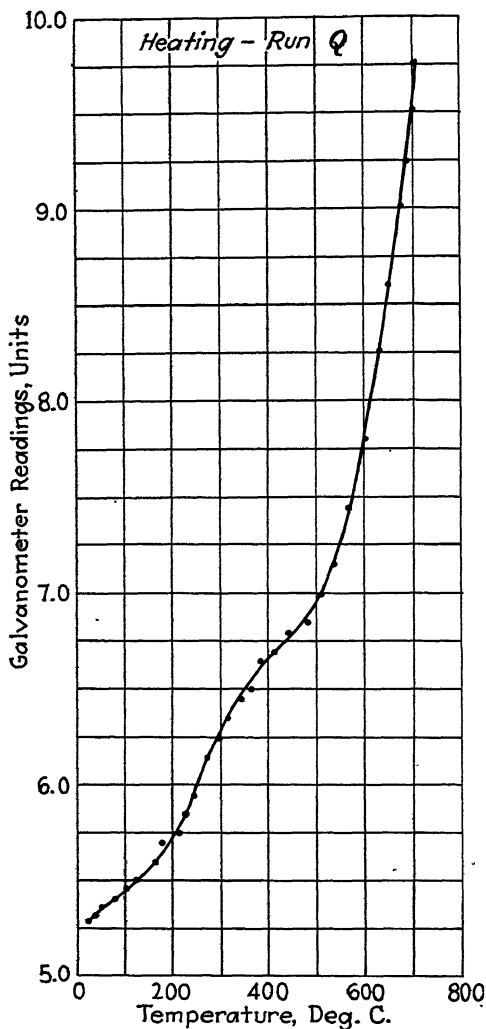
FIG. 11.—FE-SI ALLOY CONTAINING 6.48 PER CENT. SI. RELATIVE ELECTRIC RESISTANCE AT VARIOUS TEMPERATURES. GALVANOMETER READINGS CORRECTED TO 9.5 AMPERES.

which is not found in the cooling curves; this bend may be due to the fact that the furnace heated at a greater rate at this temperature than at higher temperatures, and also on cooling the specimens, the rate of cooling was slowest at about 100° to 200° C.
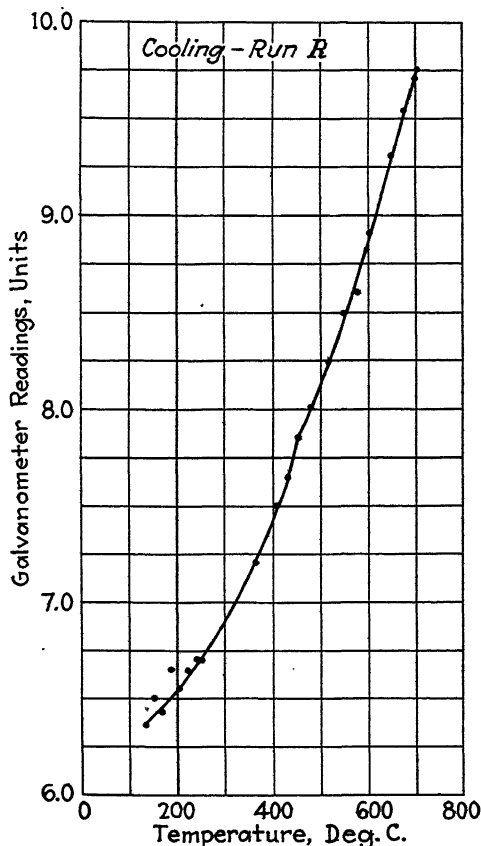
FIG. 12.—FE-SI ALLOY CONTAINING 6.48 PER CENT. SI.   RELATIVE ELECTRIC RESIST-
ANCE AT VARIOUS TEMPERATURES.   GALVANOMETER READINGS CORRECTED TO 9.5
AMPERES.

The determinations on the 4.68 per cent. silicon alloy (Figs. 13 to 18) did not give quite as consistent results as the 6.48 per cent. silicon alloy, nevertheless there was some indication of a change point in the alloy.   In run E (heating) there is a point of discontinuity at about 450° C. and in run I (heating) there is a point of discontinuity at about 350° C.; also in run E an interesting change of direction of the curve occurs below 200° C.

The electric resistance of the 4.68 per cent. silicon alloy was also tested between −15° C. and +176° C.   Only the heating curve was obtained and this curve is given in run O (Fig. 18).   A discontinuity in the curve was obtained at 104° C.   This curve was plotted to a different scale

than that used for the previously mentioned curves, because of the small range of temperature covered. The cooling curves of the 4.68 per cent. silicon alloy are given in runs F and J (Figs. 15, 17). Run F (cooling) followed run E (heating) after holding the specimen at 730° C. for approximately 10 min. A discontinuity occurred in the curve of run F at 360° C. and at a point between 500° and 600° C. The latter was con-
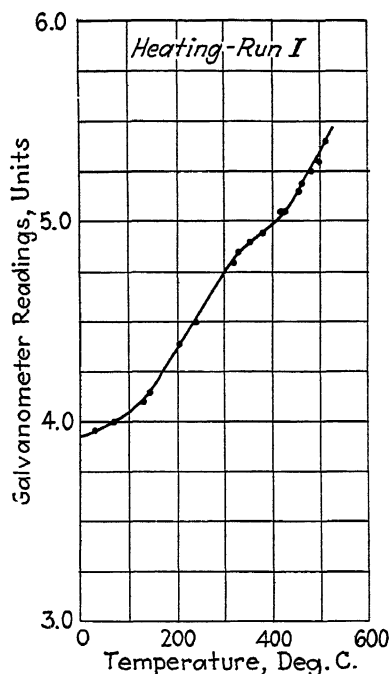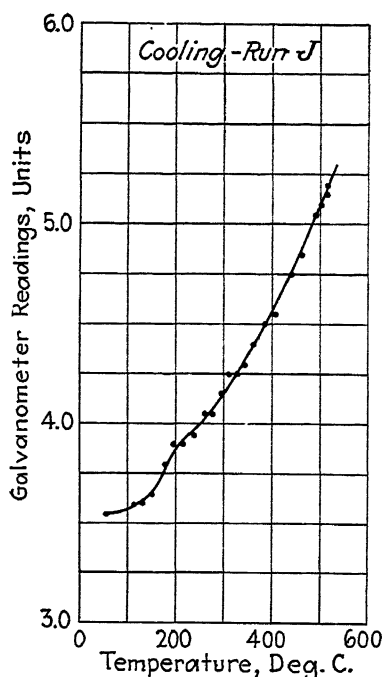

FIG. 13.—FE-SI ALLOY CONTAINING 4.68 PER CENT. SI. RELATIVE ELECTRIC RESISTANCE AT VARIOUS TEMPERATURES. GALVANOMETER READINGS CORRECTED TO 9.5 AMPERES.

firmed by run D, Fig. 13 (cooling). Run J followed run I, after the specimen had been held at 510° C. for 10 min. It will be noted that the maximum temperature of runs E and F was greater than the maximum temperature of runs I and J. The rate of cooling was approximately the same in each case. The curve of run J exhibits only one discontinuity; namely, at about 200° C.

The 2.16 per cent. silicon alloy exhibited no appreciable discontinuities in the electric-resistance curve when heated from room temperature to

791° C (Figs. 19, 20). After run G was completed, the specimen was held at temperature of about 725° C. for 10 hr. before run H (cooling) was carried out. Extremely slow heating and cooling were followed in each respective run. Run P (Fig. 21), which pertains to low temperatures, exhibited a sharp break at −90° C. in the electric-resistivity curve. This latter curve was plotted to a different scale from that of the other curves because the range of temperature was comparatively small.
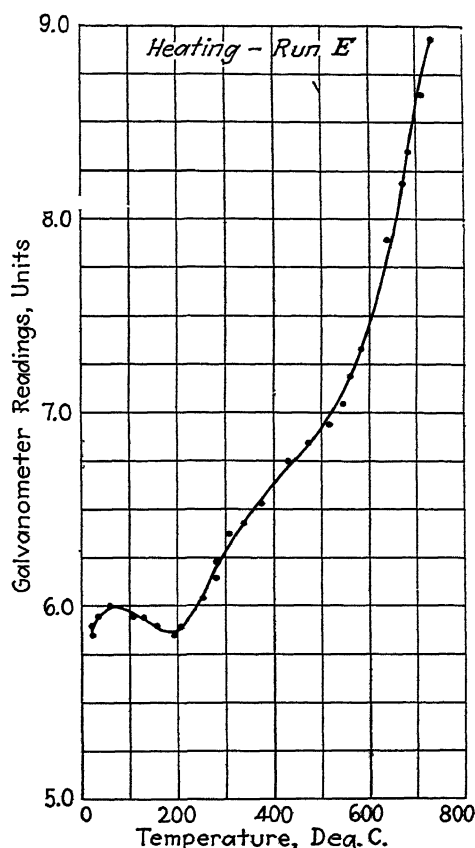
FIG. 14.—FE-SI ALLOY CONTAINING 4.68 PER CENT. SI. ELECTRIC RESISTANCE VS. TEMPERATURE. GALVANOMETER READINGS CORRECTED TO 10.0 AMPERES.

CONCLUSIONS FROM ELECTRIC-RESISTIVITY MEASUREMENTS

1. A consistent discontinuity in the temperature-electric resistance curves at 450° C. on heating and cooling in the 6.48 per cent. silicon alloy.

2. A sharp change of direction in the electric resistance curves between 500° and 600° C. in the 6.48 per cent. Si alloy on cooling.

3. The 4.68 per cent. silicon alloy exhibits a discontinuity in the electric curves at about 350° C. (taking the mean temperature from the

data on this point as given in the curves) on heating; and a discontinuity at about 300° C. on cooling (taking the mean temperature from the data on this point).

4. A much sharper change of direction occurred at 130° C. on three separate coolings, and at 98° C. as an average of three heatings of the 4.68 per cent. silicon alloy. Because run O (Fig. 18) was the most conclusive, this point (104° C.) was chosen for plotting purposes.
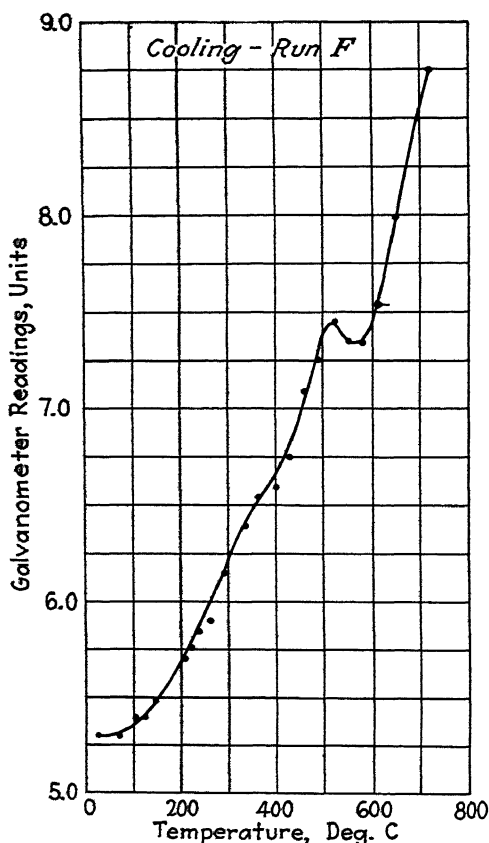
FIG. 15.—FE-SI ALLOY CONTAINING 4.68 PER CENT. SI. ELECTRIC RESISTANCE VS. TEMPERATURE. GALVANOMETER READINGS CORRECTED TO 10.0 AMPERES.

5. The 4.68 per cent. silicon alloy also shows a marked discontinuity in the temperature-electric resistance curve between 500° and 600° C. on cooling.

6. A sharp break at −90° C. was noted in the electric-resistivity curve of the 2.44 per cent. silicon alloy on heating.

7. The electric resistivity curves of the 2.16 per cent. Si alloy exhibited no discontinuities above room temperature.
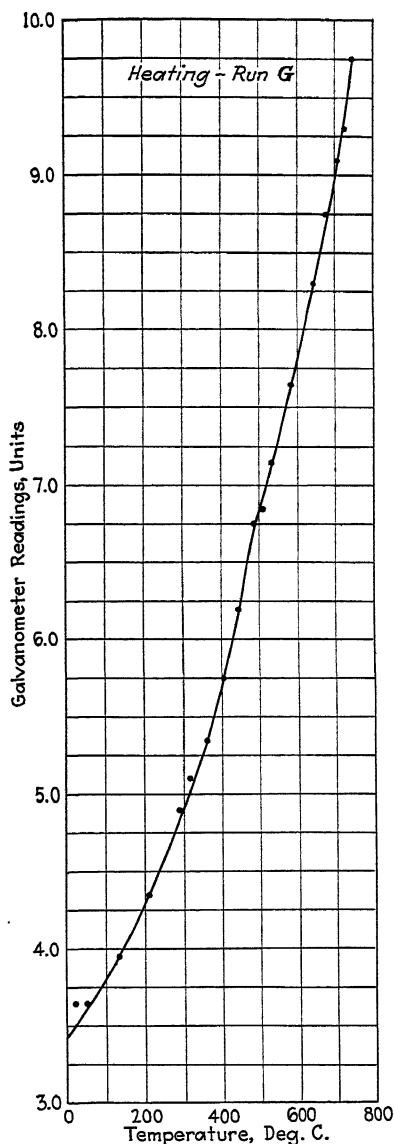
FIG. 16.—FE-SI ALLOY CONTAINING
4.68 PER CENT. SI.   RELATIVE ELECTRIC
RESISTANCE AT VARIOUS TEMPERATURES.
GALVANOMETER READINGS CORRECTED
TO 9.5 AMPERES.

FIG. 17.—FE-SI ALLOY CONTAINING
4.68 PER CENT. SI.   RELATIVE ELECTRIC
RESISTANCE AT VARIOUS TEMPERATURES.
GALVANOMETER READINGS CORRECTED
TO 9.5 AMPERES.
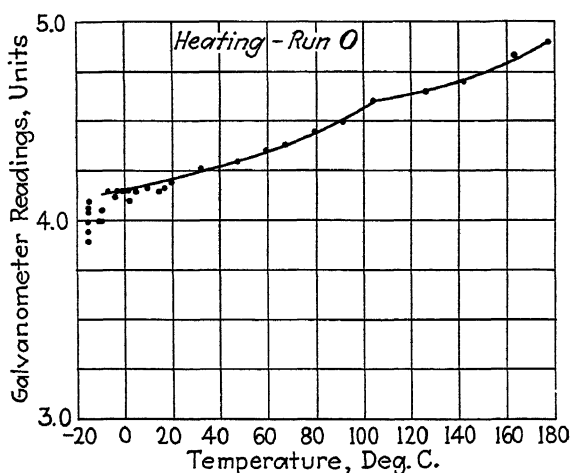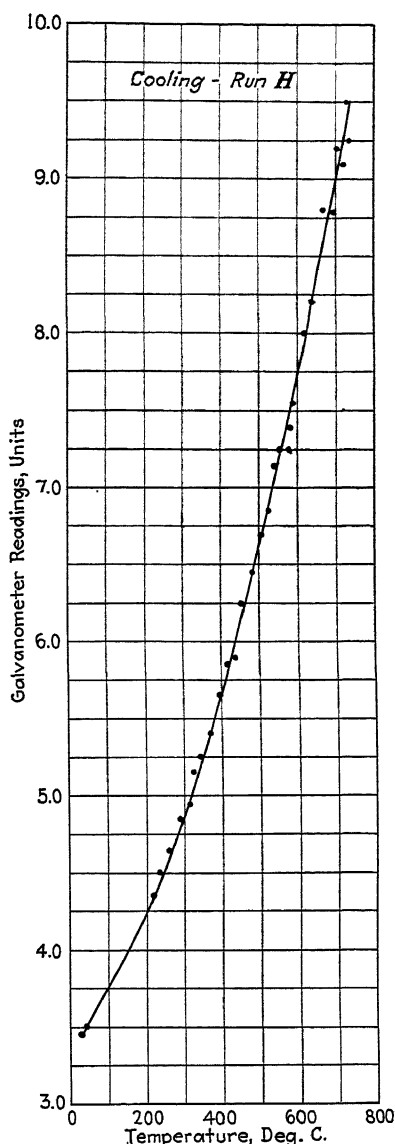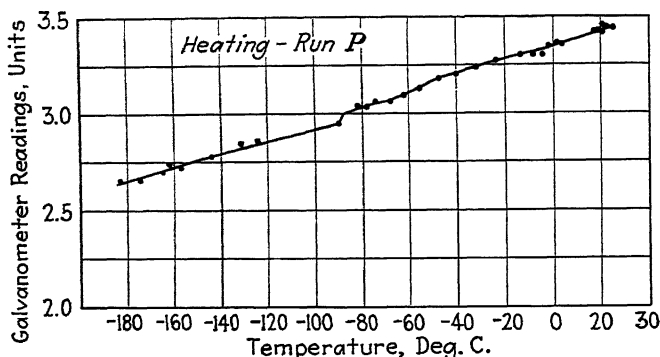

FIG. 18.—FE-SI ALLOY CONTAINING 4.68 PER CENT. AT VARIOUS TEMPERATURES.
GALVANOMETER READINGS CORRECTED TO 9.0 AMPERES.

8. The temperature-resistance curves give some fairly good proof that the line drawn by Pilling, in the iron-silicon equilibrium diagram, between the ductile and brittle alloys, represents a change of phase.

9. These conclusions are embodied in a graph in Fig. 3.

ROCKWELL HARDNESS TESTS

A series of Rockwell hardness determinations was made on some of the alloys. These results are shown in Table 2.

TABLE 2.—*Rockwell Hardness Determinations*

Si, Per Cent.	As Cast	Annealed at 1000° C. for 48 Hours	Quenched from 950° to 1000° C.	Annealed at 900° C.	Remarks
8.57	C-38	C-35	C-37		The hardness results on the quenched specimen varied considerably, probably because of small cracks in the crystals.
6.34			B-107	B-106	
4.68	C-18 (B-97) Approx.	B-101	B-84 B-91	B-95[a]	
2.44	B-90		B-82		

[a] Annealed repeatedly from about 800° C.

The chief point brought out by these hardness tests is that quenching and annealing had almost no effect on the hardness of the alloys.

MICROSCOPIC INVESTIGATION

Microscopic examination did not seem to give definite and comprehensive information on the constitution of the iron-silicon alloys to any of those who have investigated it. It was not possible to reveal the compound Fe_3Si in the various alloys that are thought to consist of the two phases, namely alpha-solid solution and Fe_3Si. Nevertheless, the latter statement does not prove that these alloys containing between 4 and 14.5 per cent. silicon are of a single phase, because there is the possibility that the etching reagent is not selective enough to attack differentially the alpha and the Fe_3Si phases.

Some of the photomicrographs are shown in Figs. 22–27. The specimens were etched with the reagent used by Corson in his work on the iron-silicon alloys, which was as follows: 2 parts glycerin (glycerol), 1 part HNO_3, 1 part HF (50–55 per cent.). The photomicrographs shown in Figs. 22 and 23 are of the cast 2.44 per cent. and 8.57 per cent. silicon alloys respectively. While both structures are polyhedral grains, there

is a marked difference in the nature of the grains.   The structures of the
6.34 per cent. and the 8.57 per cent. silicon alloys are shown in Figs.

FIG. 19.—FE-SI ALLOY CONTAINING
2.16 PER CENT. SI.   RELATIVE ELECTRIC
RESISTANCE AT VARIOUS TEMPERATURES.
GALVANOMETER READINGS CORRECTED
TO 10.5 AMPERES.

FIG. 20.—FE-SI ALLOY CONTAINING
2.16 PER CENT. SI.   RELATIVE ELECTRIC
RESISTANCE AT VARIOUS TEMPERATURES.
GALVANOMETER READINGS CORRECTED
TO 10.5 AMPERES.

24 and 27.   These alloys were heated to about 1000° C. for 1 hr. and
quenched in water.   The structures show no evidence of the "barley-

shell" markings obtained by Corson.[45] The structure of the 6.34 per cent. silicon alloy annealed from 940° C. is shown in Fig. 24. Here again no evidence of the "barley-shell" markings is present. The structure of the 8.57 per cent. silicon alloy is shown at 20 dia. in Fig. 26. Extended etching did not reveal the barley-shell markings.

The only explanation of difference in the results of Corson and those of the present investigators is that Corson used Armco iron as the base of his alloys, while electrolytic iron was used in the present investigation. There is a possibility of an electrochemical action being set up between

Fig. 21.—Fe-Si alloy containing 2.44 per cent. Si. Relative electric resistance at various temperatures. Galvanometer readings corrected to 11.0 amperes.

the small Al_2O_3 inclusions in the Armco iron and the body of the grains themselves, which would account for the strange figures obtained by Corson in his photomicrographs.

Résumé—the Iron-silicon Equilibrium Diagram

As pointed out in the first part of this paper, there is considerable disagreement concerning various parts of the iron-silicon equilibrium diagram. An attempt was made to compile and correlate the existing data on this subject (Fig. 1), and then to draw a tentative diagram as the result of this study (Figs. 2 and 3). The data on the low-silicon alloys at temperatures below 800° C. is given in Fig. 3. A magnetic transformation observed by Murakami[46] occurs at 760° C. in the 1.76 per cent. silicon alloy. This drops to 450° C. in the 17.04 per cent. silicon alloy, then remains at 450° C. in all the alloys up to 25 per cent. silicon and is slightly noticeable in the 26.90 per cent. and 27.3 per cent. silicon alloys, but could not be noticed in those higher in silicon. Murakami attributes the slight change at 450° C. in the 26.90 per cent. and 27.3 per cent.

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[45] M. G. Corson: *Op. cit.*, 266, Figs. 21 and 22.
[46] T. Murakami: *Op. cit.*

silicon alloys to insufficient annealing. The present authors observed transformations which began at about 600° C., in the 4.68 per cent. and the 6.48 per cent. silicon alloys, which are probably the same transformation points observed by Murakami but depressed because of differences
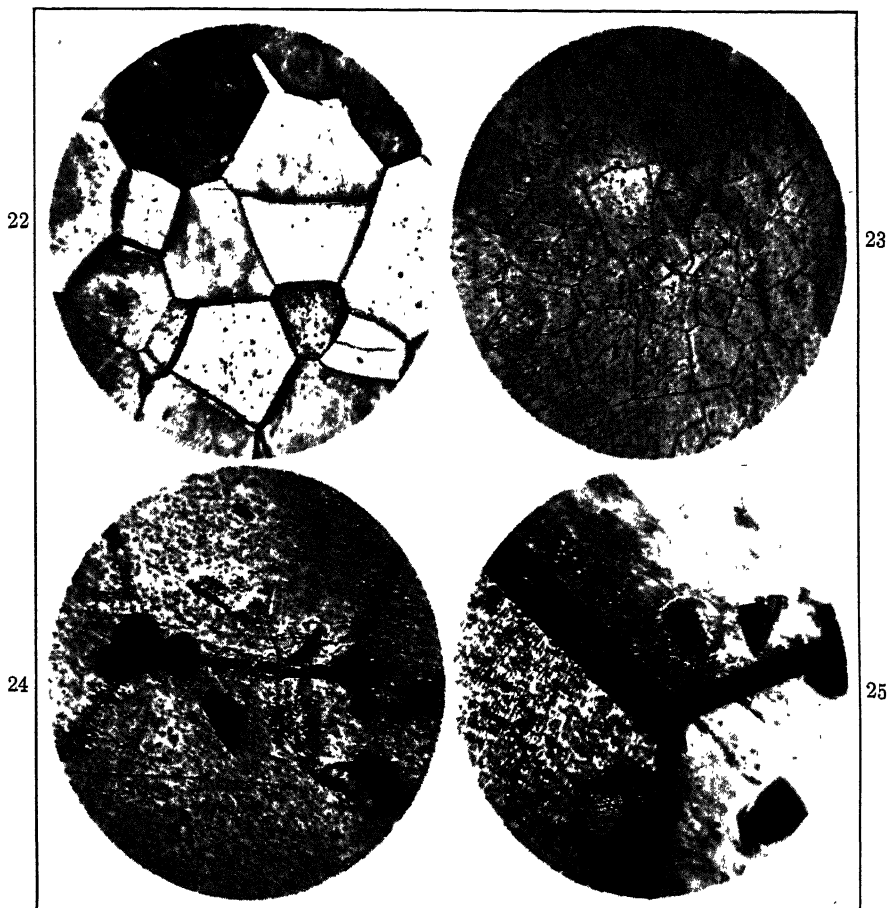
FIG. 22.—2.44 PER CENT. SI. AS CAST. × 15 (APPROX.).
FIG. 23.—8.57 PER CENT. SI. AS CAST. × 15 (APPROX.).
FIG. 24.—6.34 PER CENT. SI. ANNEALED AT 940° C. × 300.
FIG. 25.—6.34 PER CENT. SI. QUENCHED FROM 950° TO 1000° C. × 300
Reduced ⅓; original magnification given.

in method and in rate of cooling. This magnetic change observed by Murakami corresponds to the A_2 change in pure iron; the addition of silicon to iron tending to depress the temperature of the transformation.

Another interesting transformation line shown in Fig. 3 is the critical ductility temperature as determined by Pilling.[47] The latter showed that

[47] N. B. Pilling: *Op. cit.*

a sharp line of demarcation exists between the brittle and ductile iron-silicon alloys. Pilling determined this line by means of bend tests on various iron-silicon alloys containing from 0 to 4.69 per cent. silicon.
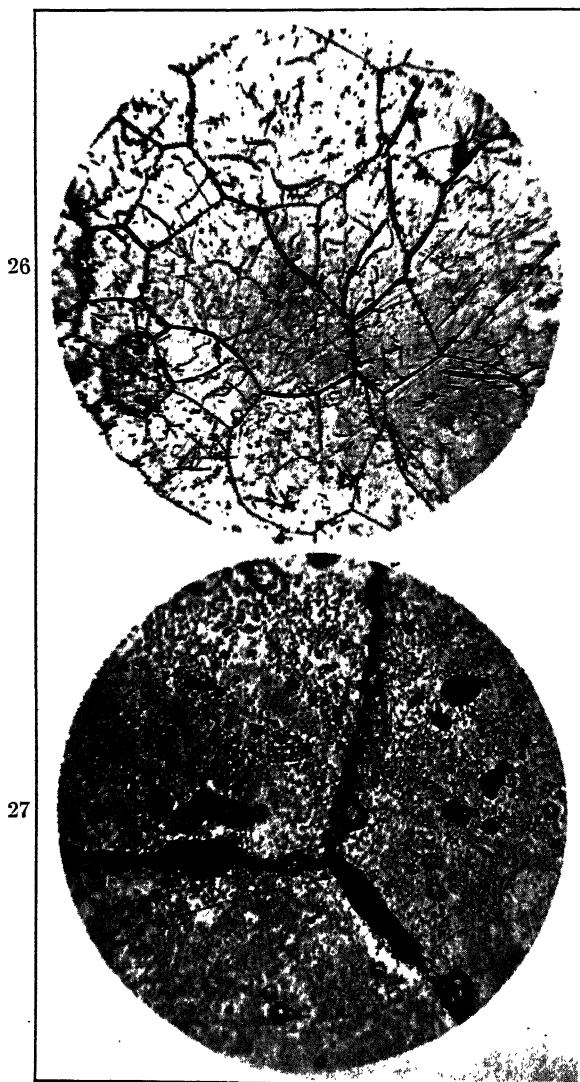
FIG. 26.—8.57 PER CENT. SI. QUENCHED FROM 1000° C. × 20.
FIG. 27.—8.57 PER CENT. SI. QUENCHED FROM 1000° C. × 300.
Reduced ⅕; original magnification given.

The present authors attempted to observe this transformation temperature by means of temperature-electric resistivity tests, and found that there is some evidence of a transformation occurring at approximately

the compositions and temperatures given by Pilling's curve. Although there were also several discontinuities in some of the temperature-resistivity curves which cannot be explained at present, the discontinuities as given by the points in Fig. 3 were rather consistent in their occurrence.

The iron-silicon equilibrium diagram as given in Fig. 2 is to be regarded as tentative only, because there are some parts, particularly the area from 0 to 15 per cent. silicon, that require further research in order to be unconditionally accepted. However, while the part of the diagram below 15 per cent. silicon is in part drawn on supposition, it does explain the brittleness of the iron-silicon alloys. The evidence for the existence of the various compounds was given earlier in this paper and will not be reviewed here.

The alloys below 33 per cent. silicon have a complicated series of transformations on cooling. The line AB (Fig. 2) has been connected with the peritectic reaction forming Fe_3Si at 1255° C. because Murakami could not observe any heat evolution corresponding to the line CD in the alloys containing less than 18.00 per cent. silicon.[48] And also because by exterpolation of the results of Pilling and those of the present authors, the curve AB connects with the peritectic reaction at point B. Nevertheless, there is a possibility that the curve AB connects with curve CD at point C instead of the peritectic reaction at B. Murakami regards the magnetic transformations FK, KG and HI as simply changes of the phase in which the lines are situated and no new phase is developed at these points. That is, he believes the line FK is a transformation in the alpha phase, while the line HI is a transformation of the compound Fe_3Si_2.

The lines separating the gamma from the alpha phases have been carefully traced by Wever and Giani,[49] Esser and Oberhoffer,[50] and also by Sanfourche.[51] Wever and Giani might be particularly mentioned for their careful and accurate determination of the boundary of the gamma phase (Fig. 2).

The diagram as drawn in Fig. 2 exhibits four compounds, each of which is a different type. The compound Fe_3Si is formed by a peritectic reaction between the melt and the solidus at B. Then a peritectoid

[48] T. Murakami: Op. cit.

[49] F. Wever and P. Giani: Beiträge zur Kenntnis des Systems Eisen-Silizium. Mitt. aus dem Kaiser-Wilhelm Inst. für Eisenforschung zur Düsseldorf (1925) 7, 59–68.

[50] H. Esser and P. Oberhoffer: Zur Kenntnis der binären System Eisen-Silizium, Eisen-Phosphor und Eisen-Mangan. Berichte der Fachausschüsse des Vereins deutscher Eisenhüttenleute (1925) Werkstoffausschuss Ber. 69, 1.

[51] M. A. Sanfourche: Op. cit.

reaction sets in at 1020° C. (line *DE*) between some of the Fe_3Si and
FeSi to form Fe_3Si_2 according to the following reaction:

$$Fe_3Si + 3FeSi \leftrightarrows 2Fe_3Si_2$$

The Fe_3Si_2 can be decomposed by heating above the line *DE* while
the Fe_3Si is decomposed when it is heated to the line *BN*. The com-
pound FeSi exhibits a maximum in its melting point curve which means
that it is not decomposed on heating. The final compound, namely
the $FeSi_2$, has a hidden maximum in its melting point curve. While it
must be remembered that there is yet some doubt as to the presence of
Fe_3Si, $FeSi_2$ and Fe_3Si_2, there is more favorable evidence than unfavorable
evidence of their presence, and in view of this fact, the compounds were
placed in the equilibrium diagram as shown in Fig. 2.

The alloys containing more than 33.3 per cent. silicon have a com-
paratively simple constitution. A eutectic occurs at 45 per cent. silicon
and an intermetallic compound at $M(FeSi_2)$. There is only 5° C.
difference between the temperature of the eutectic *P* and the melting
point of the $FeSi_2$ at *M*. The phase theta is a solid solution of $FeSi_2$ in Si.

From the preceding discussion of the equilibrium diagram of the
iron-silicon system, it is readily seen that certain parts are well estab-
lished, while other parts are somewhat doubtful. In order to understand
the effect of other elements on the constitution of the binary system
Fe-Si, it will first be necessary to thoroughly understand the constitution
of the binary system itself. There is a possibility of effecting some
radical transformations, such as changing the position of the phases in
alloys of a certain silicon content by means of adding one or more
additional elements.

SUMMARY

The existing data on the constitution of the iron-silicon alloys were
compiled and correlated, and an investigation was carried out on iron-
silicon alloys containing less than 10 per cent. silicon. This investigation
showed that discontinuities occur in the temperature-electric resistance
curves of the alloys studied and these discontinuities correspond fairly
well with the line of critical ductility in the iron-silicon equilibrium
diagram as drawn by Pilling. Micrographic and hardness tests were
made on the alloys. Finally a tentative equilibrium diagram of the iron-
silicon system was proposed.

of Metallurgical Engineering, namely Prof. Allison Butts, Prof. Gilbert E. Doan and Mr. Wilber E. Harvey, for the many helpful suggestions given during this investigation. The authors likewise desire to express their indebtedness to Dr. T. D. Yensen, research engineer, Westinghouse Elec. & Mfg. Co., for the electrolytic iron and also for copying the compiled data on the iron-silicon equilibrium diagram. Dr. F. M. Becket, vice president, Electro Metallurgical Co., most generously gave some pure silicon, which was used in part of the work.

DISCUSSION

W. E. RUDER, Schenectady, N. Y. (written discussion).—The change in the equilibrium diagram proposed by the authors is one that would be of considerable interest to all who have to do with the high-silicon sheets used in electrical apparatus, since a satisfactory explanation of the occasional brittleness of such sheets would be very welcome, but there are a number of objections to the acceptance of such a proposal.

Pilling's brittleness-temperature curve gives a true picture of approximate conditions to be met with in commercial sheets, and it has long been known that even a warming of sheets, otherwise so brittle as to be useless, would make it possible to shear, punch or form them with ease. This temperature softening requires no phase change to explain it, however, as it may be applied to a number of alloys which have brittle tendencies caused by a high content of some embrittling element. It is not solely a property of iron-silicon or similar alloys. Silicon-iron sheets with 5.5 per cent. silicon have been produced, which were quite free from brittleness at 20° C. as compared with the 4.25 per cent. silicon limit set by the Pilling-Stoughton curve. Brittleness, moreover, is an indeterminate, comparative sort of property. Pilling's method is only one way of determining this property. Whether a metal or alloy is said to be brittle or ductile is determined largely by the use to which it is to be put. To most metallurgists not accustomed to handling silicon steels, all steels with more than 2.5 per cent. silicon would be "brittle."

Should a change of phase, as suggested by the authors, exist, quenching a 5 per cent. alloy from above 200° C. should noticeably improve the ductility by maintaining Fe_3Si in solid solution. This is not the case, as we have found after many experiments. Pilling also mentions similar experiments with "if anything a decrease in ductility." Such experiments were made to test out the theory that possibly Fe_3Si might be segregated along cleavage planes under certain conditions of heat treatment, and so account for the abnormal brittleness sometimes met with, just as the authors have suggested.

An examination of the resistance-temperature curves from which the suggested phase-change boundary curve is drawn leaves much to be desired in the way of conclusive evidence. In some cases, definite discontinuations are shown, but unfortunately these are disregarded, without sufficient explanation, in favor of barely perceptible points which fall more closely on the Pilling curve. This is particularly noticeable in the case of the 4.68 per cent. and the 6.48 per cent. alloy. It would seem that the evidence in favor of the compound Fe_2Si, which the authors pass over as insufficient, were overwhelming as compared with the evidence they present in favor of their proposed change-of-phase line.

Referring again to the question of brittleness, it would be very desirable if some sort of standard of brittleness could be adopted, particularly in respect to this type of sheet steel. Pilling has used a method of his own which may have some merit,

Spooner and others have suggested the Ericson cup test, but this is quite unreliable, particularly when used with the higher silicon sheets of commerce. We have used various bend tests over standardized radii and have, at least temporarily, settled upon a radius of 5 mm. suggested by the V. D. E. In this test, sheets of standard epstein width (3 cm.) are clamped in jaws, the top edges of which have been machined to 5 mm. radius. The number of 180° bends the sheet will stand to fracture is taken as a measure of the degree of brittleness. While such a test may not be perfect, it still gives a good commercial comparison of quality in this respect, and we would urge its consideration by manufacturers and users in the interest of uniformity.

B. STOUGHTON (written discussion).—We have been very glad to receive Mr. Ruder's ideas on the proposed equilibrium diagram of the iron-silicon system, because one of the chief aims in publishing this paper was to obtain the ideas of others who are interested in the same subject. Mr. Ruder pointed out that the authors have disregarded definite discontinuities in the resistance-temperature curves, other than those corresponding to the critical ductility line as determined by Pilling. An examination of Fig. 3 will show that the discontinuities referred to by Mr. Ruder have been plotted on the diagram. The only explanation of the discontinuities, other than those corresponding to the critical ductility line, is that the change of phase, or some transformation in the nature of the alloys, which takes place when they change from ductile to brittle, or vice versa, is a rather extended transformation. This is a point that requires further research before it can be explained satisfactorily.

It may be of interest to note an observation by Dr. H. Schulz on the high-silicon structural steel, containing about 1 per cent. silicon and about 0.10 per cent. carbon.[52] Schulz found that the elongation and contraction (reduction of area) shows a remarkable increase on aging a few weeks. After aging four weeks, the average increase of elongation of the high-silicon structural steel amounted to 10 per cent., and the increase of contraction amounted to 20 per cent. This is an important observation and may indicate that an aging phenomenon takes place in iron-silicon alloys of the compositions covered by the iron-rich solid solution range.

The evidence of the presence of Fe_2Si has really been entirely of one sort; namely, the separation of Fe_2Si by chemical isolation. It has not been confirmed by micrographic, thermal, magnetic or X-ray tests, while the other compounds noted in Fig. 2 have been observed by one or more of these latter tests. Guertler and Tammann[53] showed one or more photomicrographs of iron-silicon alloys which they believed contained Fe_2Si. However, they have given up the idea that Fe_2Si is present in iron-silicon alloys, in view of later researches. Furthermore, Dr. J. L. Haughton and Dr. M. L. Becker[54] have carried out a research on the purest iron-silicon alloys that have ever been prepared for studying the equilibrium diagram of that system and have found no evidence of the compound Fe_2Si. In view of the accumulated evidence, we still maintain our belief that the presence of Fe_2Si is very doubtful in *pure* iron-silicon alloys.

T. D. YENSEN, East Pittsburgh, Pa. (written discussion).—I have examined this report on Fe-Si compounds and the accompanying equilibrium diagrams. I have been trying to consider the probability of the existence of these compounds from the point of view of the corresponding crystal structure, and I am particularly interested in Fe_3Si. If we knew all about the crystal structure of the various Fe-Si

[52] H. Schulz: Contribution to the Properties of High Silicon Steels. *Metal Ind.* [London] (1926) **29**, 134.

[53] W. Guertler and G. Tammann: *Op. cit.*

[54] J. L. Haughton and M. L. Becker: Alloys of Iron Research. Part IX. The Constitution of the Alloys of Iron with Silicon. *Jnl.* Iron and Steel Inst. (1930.)

alloys, such an analysis would be worth while, and I would suggest that the data available on this subject obtained as by X-ray analysis be collected.

It would appear from Mr. Corson's paper[55] that the original body-centered structure of Fe is retained up to 14.3 per cent. Si with a slight decrease in parameter (2.86 to 2.80 Å.) and that a new constituent begins to appear with higher silicon content. But Mr. Corson does not reveal definitely what this new structure is except to state in Appendix 1 that the body-centered structure persists even after passing the Fe_3Si point (14.3 per cent. Si). It must be assumed, therefore, that there is no sudden change of the alloy as a whole from body-centered to some other, perhaps face-centered, structure (as, for example, in the Fe-Ni alloys at about 26 per cent. Ni corresponding to Fe_3Ni). Now, Fe_3Si would mean a lattice consisting of four atoms per unit lattice, three Fe and one Si, or multiples thereof, and if the structure as a whole changed at 14.3 per cent. Si from the two-atom body-centered to the four-atom face-centered cube, this would be a good argument in favor of the existence of the compound Fe_3Si. The evidence presented by Mr. Corson, however, is all to the contrary.

He obtains 2.86 Å. as the parameter of the body-centered Fe, 2.80 for the body-centered Fe_3Si and 2.802 for alloys above 14.8 per cent. Si, also body-centered. (See Appendix 1.) It must, therefore, be taken for granted·that the 14.3 per cent. alloy has a body-centered cubic structure, and it would be interesting to find out how such a structure can be built up in multiples of 3 Fe and 1 Si atoms that would be homogeneous and regular in all directions, as must of necessity be the case for a compound. Perhaps Mr. Corson or Dr. Bain may be able to clear up this point.

No such difficulty exists in case of the alloy FeSi. This may be body-centered (FeSi) or face-centered (Fe_2Si_2) or of other form (Fe_nSi_n). Any symmetrical structure can be built up of equal numbers of atoms of two elements.

When we consider the other proposed compounds: Fe_2Si, Fe_3Si_2, $FeSi_2$, Fe_2Si_3, difficulties are again encountered in trying to arrange the atoms into a symmetrical lattice that can be termed a compound.

It seems to me that considerations of this kind should be given to a discussion of possible compounds, and I hope you will be able to consider this phase of the problem in the further work on Fe-Si alloys.

In regard to the brittleness point that was brought up, I am not so sure that there is any definite line as indicated by Mr. Pilling. We very often find iron-silicon alloys with high silicon contents, which are not brittle. Sometimes they are brittle and sometimes they are not, indicating that the brittleness is a function not of the silicon content alone but of impurities in the iron-silicon alloys.

Furthermore, magnetic transformation points are not of necessity indications of change of phase. The magnetic transformation points are points at which the thermal agitation becomes sufficient to overcome the orienting effect of the magnetic field and have nothing to do with allotropic transformations and change of phase.

G. PHRAGMÉN, Stockholm, Sweden (written discussion).—The part of the equilibrium diagram which has especially interested the authors is that with less than 30 per cent. silicon. Their diagram (Fig. 2) seems, however, not to be quite correct from the phase rule point of view. The extension of the vertical line above point C might be questionable.

The authors quote me as supporting the view that a compound Fe_3Si exists as a separate phase (p. 165). Neither my X-ray photograms nor my micrographs give any support to that view. My alloys with less than 15 per cent. silicon have been homogeneous, and the edge of the elementary cube has varied continuously with the silicon content.

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[55] M. G. Corson: *Op. cit.*

It might be said, against that, that my alloys were annealed at 1100° C., and at those temperatures there might be solid solutions of silicon in iron up to 15 per cent. silicon. The alloys were cooled in the furnace but this cooling might have been too rapid. In order to eliminate that uncertainty, I have annealed an alloy with 7.5 per cent. silicon at 600° C. for 80 hr. An X-ray photogram showed that there was only one phase present. Another specimen of the powdered alloy was annealed at 450° C. for 80 hr. and then at 380° C. for 90 hr. X-ray data showed the presence of one centered cubic phase with the lattice parameter 2844.10^{-8} cm. Thus, the presumption of a two-phase range does not seem acceptable.

When I have been dealing with the compound Fe$_3$Si, I have clearly pointed out that it is only a distinguished point in the series of solid solutions of silicon in iron. The silicon atoms substitute the iron atoms in the α-iron lattice, forming a face-centered cubic super lattice, the parameter of which is twice that of the α-iron lattice (Fig. 28).
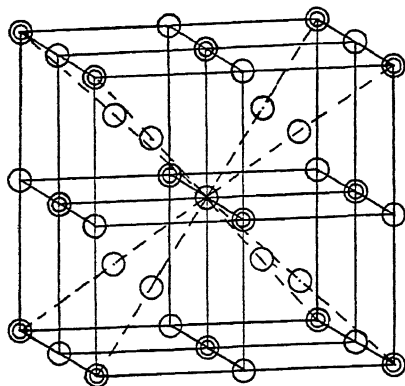
FIG. 28.—THE REGULAR DISTRIBUTION OF SUBSTITUTING SILICON ATOMS. ⊚ = SI ATOMS; ○ = FE ATOMS.

Regarding the alloys with more than 30 per cent. silicon, I will only point out a paper by J. L. Haughton and M. L. Becker at the spring meeting this year of the Iron and Steel Institute.[56] The paper mentioned is a very good verification of my previous results on the compound FeSi$_2$.

W. MERRILL, Pittsfield, Mass. (written discussion).—This paper has been of great interest to me, especially those parts dealing with the change from ductility to brittleness in silicon steel. The determination of the cause of this peculiar change is very important, especially to those working with transformer steels. The solution of the problem is difficult and it becomes especially involved when two samples of silicon steel, made in the same furnace and in the same way, of apparently identical chemical compositions and with similar heat treatments, are found to have quite dissimilar brittleness values at room temperature.

I am much inclined to doubt, from the evidence offered in this paper, that the so-called "critical ductility temperature" represents a change of phase. The authors have chosen to draw their curve (Fig. 3) through the three points representing the weakest electric-resistance changes and have almost neglected their major change points at 600°. Every one of their cooling runs, except R, indicates points of major change at 550° to 600° C. Even cooling run H would show this point if its curve

were drawn faithfully through the two points having the same galvanometer reading at 550° and 575°.

Assuming for a moment, however, that the change from ductility to brittleness in silicon steel is caused by a change of phase, it should then be possible to retain the ductile phase at room temperature, provided a sample could be quenched quickly enough from a point above the critical temperature. The curves offered by the authors do not indicate that this assumed phase change takes place instantly, and so it should be a simple matter to stabilize it at room temperatures. I have, accordingly, quenched in iced brine a number of samples of silicon steel from temperatures above the critical change temperature as indicated by the authors.

The samples used varied from 4.2 to 4.7 per cent. silicon and were in the form of strips, approximately 1 in. wide and 0.014 in. thick. Brittleness was determined at room temperature by counting the number of full 180° bends, back and forth over 5-mm. radii, the sample would stand before cracking. In all cases, the samples were placed in a furnace at the desired temperature and held 1 hr. to insure equilibrium conditions before quenching. Temperatures employed were from 200° to 900° C. in 100° steps. Results obtained are recorded in Table 3.

TABLE 3.—*Data on Samples of Silicon Steel Quenched in Iced Brine*

Sample	Silicon, Per Cent.	Brittleness, Per Cent. Quenched from								
		Sample as is	200° C.	300° C.	400° C.	500° C.	600° C.	700° C.	800° C.	900° C.
BB..........	4.75	4.1	3.6	4.0	4.1	1.6	1.6	2.4	3.4	3.5
CC..........	4.57	4.2	5.6	3.6	4.1	2.5	2.0	2.0	3.4	3.8
W..........	4.23	5.6	3.0	6.8	3.8	2.6	2.4	0.9	1.4	4.7

When one realizes that these same samples, if tested at 200° C., have a brittleness value in excess of 30, it is clearly seen that no ductile phase has been stabilized at ordinary temperatures by quenching. These results seem sufficiently convincing to eliminate the phase-change hypothesis.

The interesting result of this series of experiments is the extreme brittleness of the samples when quenched from about 600°. This is evidence, in addition to the authors' interrupted resistance-cooling curves, that an important change in the condition of silicon steel occurs at that temperature. The present authors were the first to observe any change there in low-silicon iron alloys, but more information is necessary before its exact significance is realized. The value of Messrs. Stoughton and Greiner's paper in arousing discussion on the subject of low-silicon steels cannot be denied.

I wish to acknowledge my indebtedness to the General Electric Co., in whose Pittsfield Works' laboratory my experiments were carried out, for permission to publish these results.

N. B. PILLING, Bayonne, N. J. (written discussion).—The iron-silicon alloys should deservedly excite a high degree of theoretical interest, stimulated by both their unusually diverse properties and their great technologic utility. As seems frequently to be the case, our understanding of this series has progressed much further in the direction of detailed explorations of specific properties than in the establishment of its constitution upon a sound basis. The authors are to be commended for their efforts to clarify such a fundamental problem.

The novel feature of their contribution is directed towards the alloys of low silicon content, and may be stated in a few words as proposing that the alpha solid solution, instead of extending in an unbroken series at all temperatures to the approximate

composition Fe_3Si (about 15 per cent. Si), diminishes in extent with falling temperature and precipitates this silicide along a new solubility curve which meets the 0 per cent. silicon axis at a temperature considerably below atmospheric. This curve of limiting solubility, they believe, coincides in position with that marking a great diminution in ductility which has been previously noted, and they explain the brittleness of silicon steels as having its origin in this phase change.

This interesting conception leads to at least two rather serious conflicts with other facts: (1) the observed depression of the magnetic transformation temperature of the alpha phase with rising silicon contents; (2) the identity of the ductility change in iron-silicon alloys with that occurring in iron substantially free from silicon.

The magnetic transformation temperature seems to be, not a change of phase, but the termination of a physical change within the alpha phase. As compositions lying to the right of AB in Fig. 2 would be, according to the authors' diagram, aggregates of the two phases (alpha $+ Fe_3Si$), of which the composition of the alpha phase is invariable when the temperature is fixed, the depression of the magnetic transformation temperature should cease when FK meets AB. In other words, the line AB, if it exists, should meet the line BA below K. The authors' interpretation of their data makes this a difficult accomplishment.

The brittleness which occurs at the higher temperatures in alloys with 3 to 5 per cent. silicon, and at subatmospheric temperatures with 1 to 2 per cent. silicon, seems to be identical qualitatively with the brittleness which occurs at low temperatures in almost pure iron containing not more than 0.01 per cent. silicon. The correlation of this brittleness with a silicide precipitation does not, therefore, seem to be a necessary one. The thought has been advanced before, and may be repeated, that these ductility changes may find their explanation in some property of the iron lattice, instead of in the constitution of the alloys. Silicon may modify, but probably does not initiate, the brittleness in question.

B. STOUGHTON and E. S. GREINER (written discussion).—We regret that we erroneously reported Dr. Phragmén as supporting the hypothesis of the existence of the compound Fe_3Si. Our reason for doing so was the following paragraph in his letter to us dated Sept. 25, 1929:

"The minimum of the electricity curve obtained by Corson at about 15 per cent. Si surely corresponds to the formula Fe_3Si. At this composition the distribution of the substituting Si atoms in the body-centered alpha-iron lattice will be most regular."

We wrote him on Nov. 5, 1929, replying to his letter quoted above, and said:

"According to your remarks in the letter of September 25, I will take it for granted that you agree to the presence of the compound Fe_3Si."

We had no further word from Dr. Phragmén, and we quote the paragraphs given above to show that we did not intentionally misinterpret him.

The authors, in offering the results of the research, tried to emphasize the proposals as being tentative in character, rather than a final offering of an equilibrium diagram. The purpose of the publication was to stimulate discussion and research on an important practical problem of industry. Therefore, we will not quarrel with those who point out objections to the theories advanced, but only offer our regrets that those who have raised objections to our theories have also failed to answer the objections which we have raised to the alternate theories. We are glad that the publication of this progress report on research has aroused the discussion of several able workers in this special field, and believe that the interchange of views will materially aid us in further research on the alloys of iron and silicon.

Answering Mr. Pilling, we agree that the line FK in our Fig. 2 should change direction as it crosses the line AB, and the results of Murakami[57] indicate that a

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[57] T. Murakami: *Op. cit.* Footnote 16, Table 3.

slight irregularity may occur. We do not agree that the line *AB* cannot cross the line *FK*. Furthermore, we have the argument of Yensen in the discussion of this paper, to the effect that "magnetic transformation points . . . have nothing to do with . . . change of phase." As to explaining away the ductility change in the iron-silicon alloys on the ground of its being identical with a ductility change occurring in iron substantially free from silicon at temperatures below 0° C., we find ourselves entirely unable to agree with Mr. Pilling, for the following reasons: (1) Iron containing no more than 0.01 per cent. silicon may be brittle at temperatures below 0° C. just because of that small amount of silicon, and so the argument which Pilling uses to support his thesis may actually be against it. This will be evident to anyone who considers the brittleness which equally small amounts of one element often produce in iron and other metals—phosphorus in steel, for example; or arsenic, bismuth, etc., in copper. (2) Pilling does not offer any authentic example of a marked change in ductility without a change of phase in *any* field of metallurgy. If the change is due to some property of the iron lattice, it can be demonstrated only by iron containing much less than 0.01 per cent. of silicon.

Mr. Merrill offers the argument that if the change in ductility is due to a change in phase, sufficiently rapid quenching should prevent a phase change which does not take place instantly and stabilize it at room temperatures. This, however, is contrary to some well-established examples: duralumin, for example. His experiments add information to a subject where all new data are very valuable, but they do not eliminate the phase-change hypothesis.

Influence of Nitrogen on Special Steels and Some Experiments on Casehardening with Nitrogen*

BY SHUN-ICHI SATOH,† TOKYO, JAPAN

STUDIES by many authorities have proved that nitrogen exerts an injurious influence upon iron and steel, but in the casehardening of steel by carbon, nitrogen has the advantage of accelerating the process of cementation. Its influence upon special steels is quite remarkable; it can produce the hardest layer ever known in metallurgical products—a fact hit upon by A. Fry and studied and ascertained by L. Guillet. As there have been very few investigations on the influence of nitrogen on special steels, the writer has listed important articles dealing with this problem and has conducted experiments on nitrification. He also has tested the influence of nickel upon the penetration of nitrogen in electric-arc welding.

NITROGEN PROCESS FOR SURFACE HARDENING

In 1919, Siegmon[1]‡ conducted an experiment known as "Versticken" by treating steel with ammonia gas and found that the steel thus treated has the properties of resisting corrosion. In 1922, L. E. Benson[2] nitrogenized iron and steel by sodium nitrate. Fry[3-9] studied the nitrogen process for surface hardening and published the results of his studies in 1923, 1924 and 1926. Guillet tested special steels containing various elements with the current of ammonia at 500° to 510° C.[10,11,12], and determined the hardness of some of them at various temperatures.[13] He also conducted corrosion tests[14] in 1927. Fry[15] stated that tinplating could prevent nitrogen from penetrating into steel in the course of nitrification. In 1927, Guillet[65] described the historical notes of the nitrification; and many applications of nitrification were published in the *Kruppsche Monatshefte*.[51,59,62,63,64,74,75] H. K. Herschman[66] conducted the wear test of the nitrified steel. Gunnar Hägg investigated

the nitrified layer by means of X-ray.[70]   The etching test with copper sulfate solution and the corrosion test were reported by O. Hengstenberg.[71] R. H. Hobrock[73] measured the volume change caused by the nitrification.

The writer has tested, with the current of ammonia at 580° C., electrolytic iron, iron containing aluminum, titanium and manganese, and chrome steel (C, 0.1 to 0.2 per cent.; Cr, 1 to 2 per cent.) containing aluminum, titanium, manganese, zirconium, molybdenum, tungsten and vanadium.   Special steels containing boron, magnesium, copper and cerium were also tested, but no results worth reporting were obtained (see appendixes).

The author prepared special steels by melting electrolytic iron and other elements in the Tammann furnace and then tested their forgeability by heating and hammering them.   He tested the special steels thus prepared with ammonia gas at 580° C. for $4\frac{1}{2}$ hr. in the electric resistance furnace and cooled them slowly.   He determined the Brinell hardness before and after this treatment, using a 1-mm. ball and a 30-kg. load.   He believes, as Fry[8] and Guillet[10] pointed out, that the Brinell hardness tests may show incorrect results when the hardness of hardened metals is too great.   Chrome steels including those containing titanium, aluminum and zirconium were next tested with the current of ammonia at 560° C. for 15 hr.   The Brinell hardness of each of these steels was determined at the end of every 5-hr. period of treatment, and tension tests were conducted on some of them.

Effect of Carbon on the Nitrified Steel

The injurious effect of nitrogen on steel is said to become greater as the carbon content increases.[16,17,18]   Nitrogen has the property of retaining iron in gamma modification and consequently of retaining carbon in the form of the solid solution;[19,20,21] i. e., of lowering the A_1 point.[20]   In the nitrogenization of steel by sodium nitrate, it is difficult to force nitrogen into high-carbon steel.   This difficulty of penetration is caused not so much by the presence of the pearlitic areas as by the presence of a greater quantity of the solid solution of carbon than is ordinarily seen in alpha iron.[2]   The container used in Haber's process, on the other hand, is subject to marked decarburization[22,23] while ammonia gas is being prepared in it.   Some believe that carbon in steel resists the penetration of ammonia gas;[23,24] others contradict this.[24,25] Very recently, it was proposed that the quantity of carbon content in the container used in the Haber method should not exceed 0.3 per cent.[26] In the nitrogen process for surface hardening, according to Guillet,[10] the more carbon there is in the steel the greater will be the hardness, but Fry's opinion[6] is entirely contrary.   In view of these facts, the writer used chiefly steel of 0.1 to 0.2 per cent. carbon content in his experiments.

Effect of Chromium on the Nitrified Steel

Chromium nitride has been known for many years.[27,28]   When metallic chromium is heated in nitrogen gas[29,30] or ammonia gas,[30] the compound CrN is formed.   Baur and Vörmann[31] measured the dissociation pressure of this compound.   When alloy steel containing chromium is heated in nitrogen gas, its nitrogen content increases.[32,33,34] Steel containing chromium when heated *in vacuo* evolves more nitrogen than other alloy steels.[35]   It is evident that chromium has great affinity for nitrogen.[36,37]   Nitride of chromium has the property of preventing hydrogen or ammonia from penetrating into the steel.[23,26]   It is for this reason that the Haber container made of chrome vanadium steel produced the best result.[23,24]   Recently the minimum quantity of chromium content in this alloy steel was decided to be 2.25 per cent.[26]   In the nitrogen process for surface hardening, chromium has effective properties and the chrome steel has therefore been frequently used for this purpose.[3, 6,7,8,10,13,14]   The writer tested a few chrome steels with the current of ammonia at 580° C. for 4½ hr. and then cooled them slowly in the furnace.   The results are indicated in Table 1.   Treatments described hereafter are the same as the one just mentioned, unless otherwise noted.

TABLE 1.—*Tests on Iron and Chrome Steel*

Current of ammonia at 580° C. for 4½ hr.   Cooled slowly in furnace.

Number of Steel	Chemical Analysis		Brinell Hardness		
	C, Per Cent.	Cr, Per Cent.	Before Treatment	After Treatment	Difference
Electrolytic iron					
9	0.050		118	105	−13
Cr steel					
76	0.120	0.612	142	248	106
1	0.185	0.855	108	370	262
77	0.065	1.128	123	352	229
78	0.274	1.938	229	477	248

As may be seen from Table 1, the increase of carbon and chromium brings about the greater hardness.   In this experiment chrome steels (Cr, 1 to 2 per cent.; C, 0.1 to 0.2 per cent.) were used together with other elements.

Effect of Aluminum on the Nitrified Steel

Aluminum combines with nitrogen[25] to form AlN[25,29] when it is heated in nitrogen gas; AlN is stable up to the temperature of 1750° C.[25]

Aluminum combines with ammonia gas but this reaction falls short to form AlN.[29] Nitride of aluminum is capable of being dissolved in iron as a solid solution, and when dissolved thus, it increases the nitrogen content of the iron.[25] In the nitrogen process for surface hardening, aluminum, which has great affinity for nitrogen,[33,36] increases markedly the hardness of the steel nitrified.[3,6,7,10,13] In 1928, Guillet[69] reported the important application of the nitrified aluminum steel in the aircraft and automotive industry. Kinzel[72] tested the steel cemented by aluminum with the current of ammonia. The writer tested a number of aluminum steels. The maximum quantity of aluminum in steel that
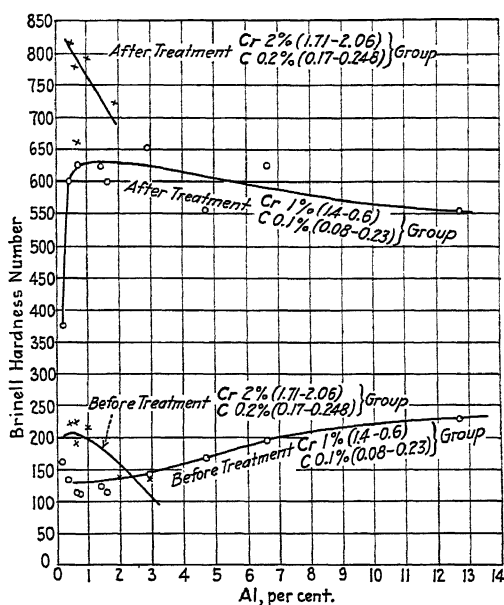
FIG. 1.—RELATION BETWEEN ALUMINUM CONTENT AND BRINELL HARDNESS OF STEEL.

may be forged well is determined to be 10.5 per cent. Al.[50] The writer tested iron containing aluminum and chrome steel containing various quantities of aluminum up to 10 per cent., with ammonia in the usual way, the results of which are shown in Table 2. With the object of ascertaining the relationship between the aluminum contents and their respective hardness, the writer drew, as given in Fig. 1, curved lines whose ordinates indicate the Brinell hardness and abscissas the aluminum contents. From these curves we can see that at 0.6 to 0.7 per cent. Al the nitrified steel has its maximum hardness. The four curves in Fig. 1, as well as in Fig. 2, consist of two curves of about 1 per cent. chromium content and those of about 2 per cent. chromium content.

TABLE 2.—*Tests on Steels Containing Aluminum*

Number of Steel	Chemical Analysis			Brinell Hardness		
	C, Per Cent.	Cr, Per Cent.	Al, Per Cent.	Before Treatment	After Treatment	Difference
Al steel						
14	0.055		0.465	121	212	91
Cr-Al steel						
34	0.090	1.092	0.208	159	375	216
35	0.109	1.409	0.409	134	601	467
83–86	0.109	1.069	0.578	116	706	590
19	0.095	1.272	0.731	121	625	505
20	0.183	1.081	1.410	126	626	500
63	0.234	1.012	1.617	113	601	488
21	0.150	0.998	2.910	146	654	508
22	0.131	0.875	4.719	170	555	385
23	0.103	1.204	6.592	197	626	429
24	0.082	0.663	12.705	229	577	348
65	0.248	1.710	0.556	241	815	574
87–90	0.169	2.031	0.616	189	658	469
68	0.205	2.060	0.622	223	779	556
69	0.217	2.015	1.012	217	795	578
70	0.217	2.015	1.927	136	725	589
71	0.191	1.938	2.916	142	522	380

Effect of Titanium on the Nitrified Steel

Titanium combines with nitrogen to form stable compounds of TiN_2, Ti_3N_4, Ti_5N_6.[38] It has great affinity for nitrogen[33,34,40] and can burn in nitrogen gas.[39] The nitrides thus formed are stable up to the temperature of 1750° C.[41,42] The nitride TiN[29,30] is a very hard substance, its hardness being[43] 9 to 10. These nitrides are soluble in iron as a solid solution.[42] When we melt ferrotitanium its nitrogen content increases 5 to 9 times.[34] Therefore the time for melting titanium-vanadium steel should be as short as possible.[42] Titanium steel has been used in the nitrogen process for surface hardening.[6,14] The writer tested a number of titanium steels. Venetor[52] said that maximum titanium content that permits of forging is 0.35 to 0.5 per cent. According to Guillet,[53] it is difficult to mix over 3 per cent. of titanium in steel. The writer tested in the ordinary way the titanium steel and chrome steel (Cr, 1 to 2 per cent.; C, 0.1 to 0.2 per cent.) with varying quantities of titanium and with the current of ammonia. The results are shown in Table 3. The relationship between the titanium contents and their respective hardness is shown in Fig. 2. We see from the curves that the hardness increases as the titanium content increases but over 3 per cent. of titanium gives the metal a brittle layer that can be easily scratched off.
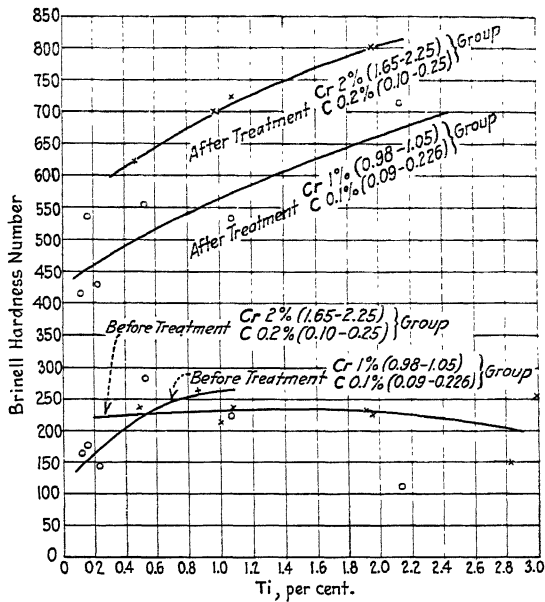
FIG. 2.—RELATION BETWEEN TITANIUM CONTENT AND BRINELL HARDNESS OF STEEL.

TABLE 3.—*Tests on Titanium Steels*

Number of Steel	Chemical Analysis			Brinell Hardness		
	C, Per Cent.	Cr, Per Cent.	Ti, Per Cent.	Before Treatment	After Treatment	Difference
Ti steel						
46	0.002		2.502	134	712	578
Cr-Ti steel						
36	0.104	1.039	0.125	163	415	252
28	0.087	0.977	0.178	177	534	357
37	0.131	1.030	0.225	146	429	280
29	0.226	0.998	0.532	285	555	270
30	0.155	1.094	1.065	223	534	311
64	0.038	0.901	2.126	113	712	599
72	0.164	2.015	0.471	235	626	391
66	0.254	2.246	1.000	212	700	688
73	0.199	1.985	1.088	235	725	490
74	0.254	1.969	1.934	229	601	372
91	0.181	2.015	1.952	126	800	674
75	0.169	1.969	2.830	152	591	439

Effect of Aluminum and Titanium on Nitrified Steel

As aluminum and titanium produced the hardest layers, the writer tested special steels containing both elements. The results are shown in

Table 4. The hardness thus obtained was not so great as he had expected it to be.

TABLE 4.—*Tests on Chrome Steel Containing Aluminum and Titanium*

No. of Steel	Chemical Analysis				Brinell Hardness		
	C, Per Cent.	Cr, Per Cent.	Al, Per Cent.	Ti, Per Cent.	Before Treatment	After Treatment	Difference
58	0.079	1.368	1.400	0.500	352	626	274
59	0.098	1.563	6.279	2.627	217	712	495
67	0.434	2.383	4.221	2.001	142	779	637

Effect of Manganese on Nitrified Steel

Nitride of manganese has been known for many years.[28]   Manganese unites directly with nitrogen to form Mn_5N_2[25,44] and with ammonia to form Mn_3N_5.[25,29,30]   This shows that manganese has great affinity for nitrogen.[25,33,36,40,46]   The nitride of manganese is stable even at 1000° C.[25]   It is soluble in iron as a solid solution and increases the nitrogen content of the iron.[25,42,44]   Studies have been made by some persons on the influence of nitrogen upon manganese steel.[23,25,37]   Nitrogenization of iron and steel by sodium nitrate is hindered by the presence of manganese,[2] therefore manganese is a convenient element to produce a hard layer only at the surface of the nitrified steel.   The manganese steel has already been used in the nitrogen process for surface hardening.[10,14]   The writer tested manganese steel and chrome steel containing various percentages of manganese in the usual way, the results of which are shown in Table 5.

TABLE 5.—*Tests on Manganese Steels*

Number of Steel	Chemical Analysis			Brinell Hardness		
	C, Per Cent.	Cr, Per Cent.	Mn, Per Cent.	Before Treatment	After Treatment	Difference
Mn steel						
45	0.043		1.231	131	212	81
Cr-Mn steel						
43	0.074	0.752	0.021	152	341	189
44	0.098	0.766	0.455	116	363	247
38	0.079	0.868	0.508	163	388	255
39	0.106	1.108	2.062	285	514	229
40	0.134	0.718	3.749	321	495	174
41	0.180	0.786	5.760	363	460	97

Effect of Tungsten on Nitrified Steel

Tungsten does not combine with either nitrogen[29,33,38] or ammonia[24,30] even at a high temperature. It has no effect upon the hardness.[10] As Guillet[14] obtained a noteworthy result on the chrome-tungsten-vanadium steel, the writer tested some tungsten steel. Up to 30 per cent. the tungsten steel is forgeable[54] but he tested 3 per cent. tungsten steel as Guillet[14] did. Table 6 shows the results.

TABLE 6.—*Tests on Chrome-tungsten Steel*

Number of Steel	Chemical Analysis			Brinell Hardness		
	C, Per Cent.	Cr, Per Cent.	W, Per Cent.	Before Treatment	After Treatment	Difference
60	0.074	0.738	1.031	187	429	242
56	0.174	0.732	2.918	235	514	297

Effect of Molybdenum on Nitrified Steel

Some say molybdenum does not combine with nitrogen at a high temperature[33,38] but absorbs nitrogen when the latter is compressed,[29] while others believe that there is no definite nitride of molybdenum.[30] The container used in Haber's process is often made of molybdenum steel.[23] Molybdenum steel is used in the nitrogen process for surface hardening.[10] The writer tested this type of steel, with the results which are shown in Table 7.

TABLE 7.—*Tests on Chrome-molybdenum Steel*

Number of Steel	Chemical Analysis			Brinell Hardness		
	C, Per Cent.	Cr, Per Cent.	Mo, Per Cent.	Before Treatment	After Treatment	Difference
47	0.125	0.800	1.200	206	401	195
48	0.125	0.992	2.400	311	601	290

Effect of Zirconium on Nitrified Steel

Zirconium reacts with nitrogen at 1100° C. to form stable compounds Zr_3N_2.[29,30] There are besides Zr_2N_3[30] and ZrN.[40] The hardness of ZrN is 8 to 9,[53] which shows that zirconium is an effective element to give great hardness to steel. Moreover, zirconium is placed just under titanium in the periodic table and we can well imagine from this that it

will give steel great hardness. Zirconium steel was tested by Kinzel[72] for nitrification. His description of his work was published at the same time that the author's present paper appeared in Japan. The writer tested chrome steel containing zirconium in the usual way. The results, in Table 8, show a marked increase in hardness.

TABLE 8.—*Tests on Chrome-zirconium Steel*

Number of Steel	Chemical Analysis			Brinell Hardness		
	C, Per Cent.	Cr, Per Cent.	Zr, Per Cent.	Before Treatment	After Treatment	Difference
53	0.136	0.926	0.068	166	415	249
54	0.180	0.848	0.068	146	514	368

TABLE 9.—*Test on Chrome-uranium Steel*

Number of Steel	Chemical Analysis			Brinell Hardness		
	C, Per Cent.	Cr, Per Cent.	U, Per Cent.	Before Treatment	After Treatment	Difference
50	0.198	0.752	1.145	262	534	272

Effect of Uranium on Nitrified Steel

Uranium combines with nitrogen at 1000° C. and with ammonia at a lower temperature, to form stable nitride.[29,30]   Guillet [14] tested the uranium steel for nitrification. The writer tested chrome steel containing uranium in the usual way. The results are shown in Table 9.
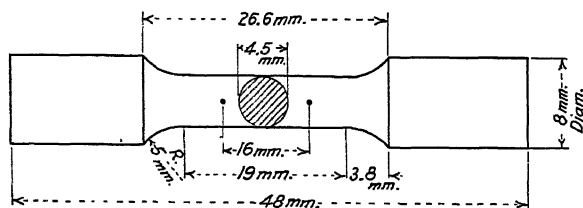
FIG. 3.—FORM OF SPECIMEN USED IN TENSION TESTS.

Tension Tests of Chrome-aluminum Steels

The writer conducted tension tests of some chrome steel containing aluminum which becomes very hard when nitrified. The results are shown in Table 10. Fig. 3 shows the form of the specimen used in the tests.

TABLE 10.—*Tests on Chrome-aluminum Steel*

Number of Steel	Chemical Analysis			Tensile Strength, Kg. per Sq. Mm.	Elongation in 2 In., Per Cent.	Brinell Hardness before Treatment
	C, Per Cent.	Cr, Per Cent.	Al, Per Cent.			
86	0.109	1.069	0.578	40.9	26.3	116
89	0.169	2.031	0.615	48.3	32.5	189

Relationship between Time of Treatment and Hardness of Nitrified Steels

The experiments described above were conducted at 580° C. for 4½ hr. Seven specimens were tested at 560° C. for 15 hr. and the Brinell hardness was determined at the end of every 5-hr. period of treatment. The first 5 hr. showed some increase in hardness but after this the hardness remained practically the same. The results are shown in Table 11.

TABLE 11.—*Tests at 560° C. for 15 Hours*

Number of Steel	Type of Steel	Chemical Analysis					Brinell Hardness				
		C, Per Cent.	Cr, Per Cent.	Al, Per Cent.	Ti, Per Cent.	Zr, Per Cent.	Before Treatment	At End of 4.5 Hr.	At End of 9.5 Hr.	At End of 14.5 Hr.	At End of 19.5 Hr.
54	Cr-Zr	0.180	0.848			0.068	146	514	555	522	
85	Cr-Al	0.109	1.069	0.578			116	706	779	693	745
20	Cr-Al	0.183	1.081	1.410			126	626	693	758	665
29	Cr-Ti	0.226	0.998		0.532		285	555	555	522	503
37	Cr-Ti	0.131	1.030		0.225		146	429	534	503	495
66	Cr-Ti	0.155	1.094		1.065		212	700	665	522	543
77	Cr	0.065	1.128				123	352	421	396	375

Photomicrographs

The photomicrographs of chrome steel containing aluminum, titanium manganese, tungsten, zirconium and uranium before and after treatments are shown in Figs. 4 to 19. The specimens were etched with alcoholic picric acid. The left sides of the photomicrographs show the edges of the specimens.

EFFECT OF NICKEL ON PENETRATION OF NITROGEN IN ELECTRIC-ARC WELDING

Whether nickel, with which the electrode is plated, prevents the penetration of atmospheric nitrogen in the arc-fused metal or not is considered to be one of the problems of the influence of nitrogen upon alloy steels. In fact, in steel deposited from a nickel-plated iron electrode with a coating containing small quantities of carborundum, silica and
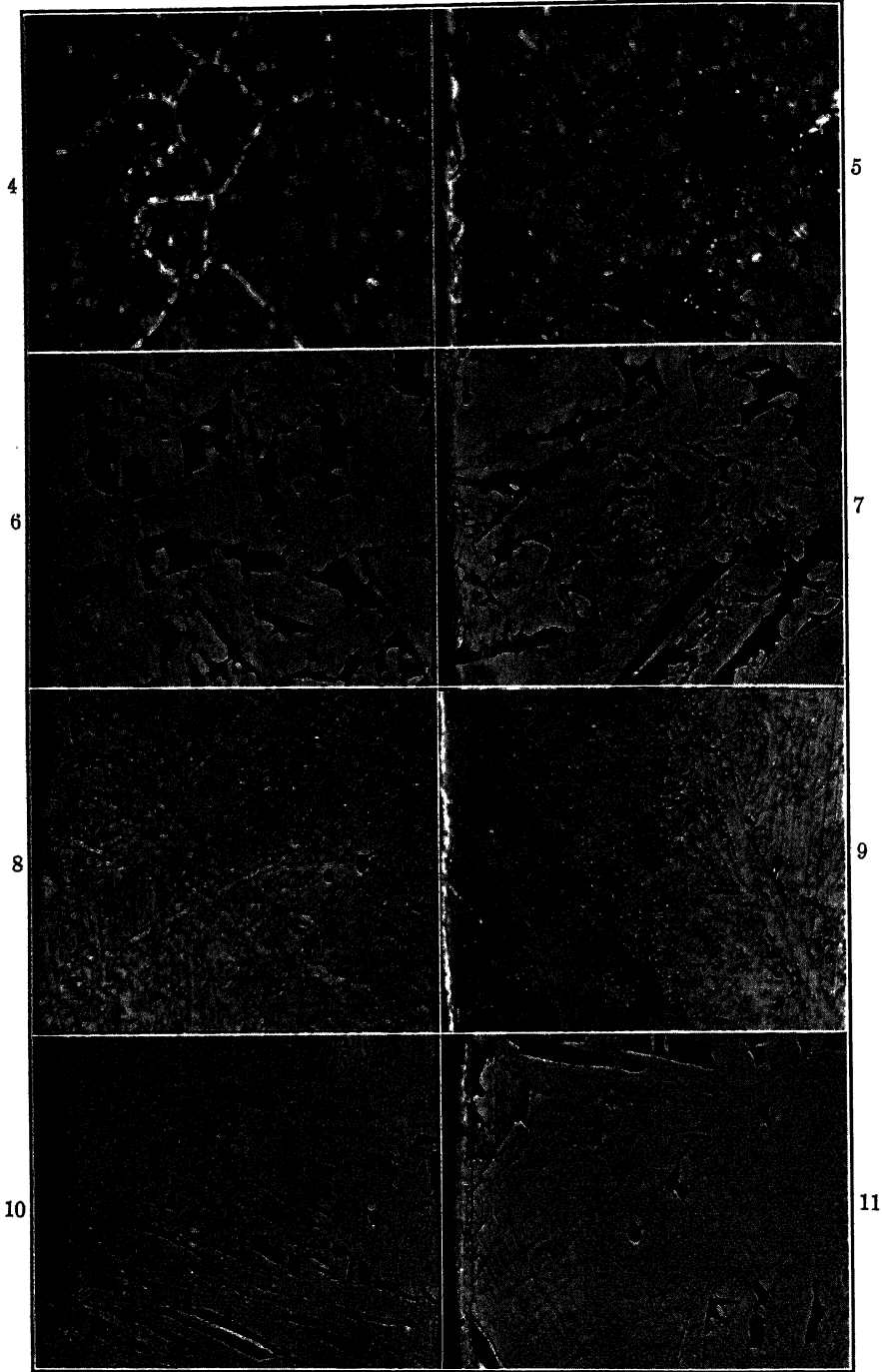
FIGS. 4–11 — ✕ 150.   (CAPTIONS ON OPPOSITE PAGE.)

barium carbonate, we see very few nitrogen needles under the microscope. With the object of finding the cause of this phenomenon, the writer made four electrodes and from these electrodes deposited four kinds of steel. He then analyzed each of these deposits according to the method of Hurum and Fay,[48] using a transparent quartz tube like that described by Sawyer,[49] and obtained the following results:

1. Deposit from iron bar without coating or plating contained 0.116 per cent. N_2

2. Deposit from electrode 1 with 1 g. Ni plated contained 0.138 per cent. N_2

3. Deposit from electrode 1 with coating contained 0.078 per cent N_2.

4. Deposit from electrode 2 with coating contained 0.068 per cent. N_2.

From these results we may see that nickel has no power to prevent atmospheric nitrogen from penetrating into the deposit. The fact that in the steel deposited from electrode 4 we discover, under the microscope, almost no needle, shows the properties of nickel of retaining nitrogen in ferrite in the form of a solid solution.[37]

As stated by Fry[6] and Guillet,[10] nickel has no property to produce the surface-hardening effect of nitrogen. The writer therefore thinks this new phenomenon of nickel in welding will be applied hereafter.

SUMMARY

The writer collected important papers dealing with the influence of nitrogen on special steels. He tested special steels containing chromium, aluminum, titanium, manganese, zirconium, molybdenum, tungsten and uranium with the current of ammonia at 580° C. and 560° C., and determined the Brinell hardness by tests upon each steel before and after the treatment; he determined the relationship between the different elements and their respective powers of giving hardness to steel and found that aluminum and titanium gave the hardest layers; then he conducted tension tests of some of these steels. Photomicrographs of the various specimens before and after the treatment are shown. He next tested the influence of nickel upon the penetration of nitrogen in electric-arc welding.

FIG. 4.—No. 50 BEFORE TREATMENT. HARDNESS, 262.
C, 0.198 per cent.; Cr, 0.752; U, 1.145.
FIG. 5.—No. 50 AFTER TREATMENT. HARDNESS, 534.
FIG. 6.—No. 54 BEFORE TREATMENT. HARDNESS, 146.
C, 0.180 per cent.; Cr, 0.848; Zr, 0.068.
FIG. 7.—No. 54 AFTER TREATMENT. HARDNESS, 514.
FIG. 8.—No. 56 BEFORE TREATMENT. HARDNESS, 235.
C, 0.174 per cent.; Cr, 0.732; W, 2.918.
FIG. 9.—No. 56 AFTER TREATMENT. HARDNESS, 514.
FIG. 10.—No. 44 BEFORE TREATMENT. HARDNESS, 116.
C, 0.098 per cent.; Cr, 0.766; Mn, 0.455.
FIG. 11.—No. 44 AFTER TREATMENT. HARDNESS, 363.
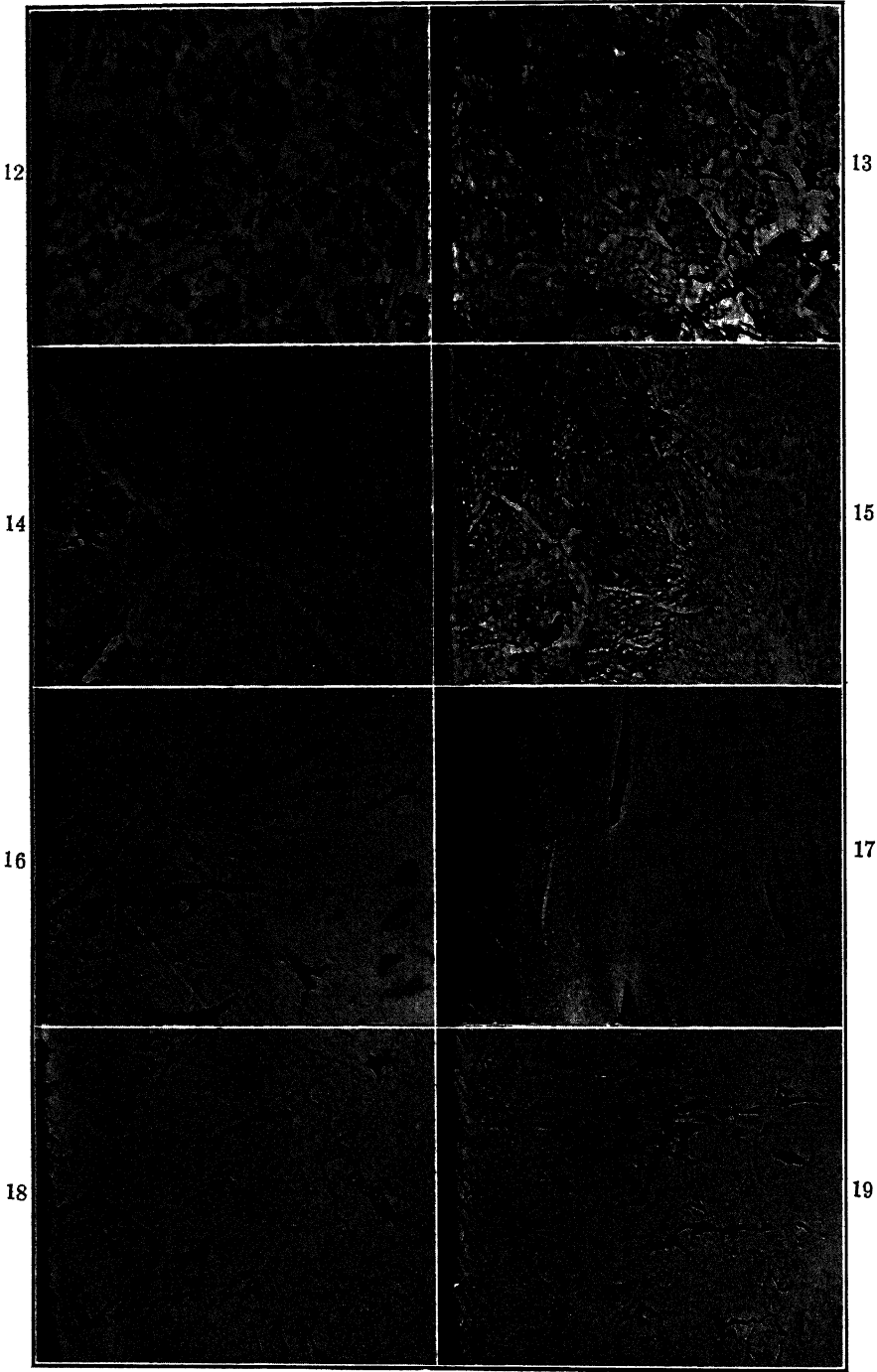
FIGS. 12–19.— × 150.   (CAPTIONS ON OPPOSITE PAGE.)

APPENDIXES

Effect of Boron on Nitrified Steel

Boron combines directly with nitrogen to form BN.[29,30,43,47] Campbell and Fay[55] have conducted the cementation by boron, which shows that the specimen thus cemented absorbed more nitrogen than that which was cemented by carbon. On the specimen that absorbed nitrogen was found a brittle layer that could be easily scratched off. Smith[36] has reported the boron treatment of nitrogen in steel. No one has tested boron steel for nitrification. As the largest permissible percentage of boron[57] for forging is 0.8 per cent., the writer mixed boron within this limit with chrome steel and tested it. He obtained no trustworthy chemical analyses; the test specimen contained 0.159 per cent. C and about 1 per cent. Cr. Brinell hardness before treatment was 152; after treatment, 277; difference, 125.

Effect of Magnesium on Nitrified Steel

Magnesium combines directly with nitrogen to form Mg_5N_2.[29,30] Magnesium is placed very near to boron and aluminum in the periodic table, therefore, supposing it may have a good effect upon the hardness, the writer tested its effect in this respect, but, as shown in Table 12, no magnesium alloy of high percentage was obtained.

TABLE 12.—*Test on Magnesium Steels*

Number of Steel	Chemical Analysis			Brinell Hardness		
	C, Per Cent.	Cr, Per Cent.	Mg, Per Cent.	Before Treatment	After Treatment	Difference
Mg steel						
79	0.087		0.026	111	125	14
80	0.044		0.014	136	126	−10
82	0.038		0.009	107	118	11
Cr-Mg steel						
81	0.166	1.230	0.015	149	352	203

FIG. 12.—No. 29 BEFORE TREATMENT. HARDNESS, 285.
C, 0.226 per cent.; Cr, 0.998; Ti, 0.532.
FIG. 13.—No. 29 AFTER TREATMENT. HARDNESS, 555.
FIG. 14.—No. 72 BEFORE TREATMENT. HARDNESS, 235.
C, 0.164 per cent.; Cr, 2.015; Ti, 0.471.
FIG. 15.—No. 72 AFTER TREATMENT. HARDNESS, 626.
FIG. 16.—No. 21 BEFORE TREATMENT. HARDNESS, 146.
C, 0.150 per cent.; Cr, 0.998; Al, 2.910.
FIG. 17.—No. 21 AFTER TREATMENT. HARDNESS, 654.
FIG. 18.—No. 58 BEFORE TREATMENT. HARDNESS, 352.
C, 0.079 per cent.; Cr, 1.368; Al, 1.40; Ti, 0.50.
FIG. 19.—No. 58 AFTER TREATMENT. HARDNESS, 626.

Effect of Copper on Nitrified Steel

Nitride of copper (Cu_3N) is obtained by the reaction of copper oxide and ammonia.[30] The superior limit of the percentage of copper that permits forging is 7 per cent.[58] The writer tested the copper steels but did not analyze them. Table 13 shows results of the hardness test.

TABLE 13.—*Tests on Copper Steels*

Number of Steel	Percentage before Melting				Brinell Hardness		
	C, Per Cent.	Cr, Per Cent.	Cu, Per Cent.	Al, Per Cent.	Before Treatment	After Treatment	Difference
Cr-Cu steel							
4	about 0.1	about 1	about 0.6		144	547	403
5	about 0.1	about 1	about 1.2		163	154	−9
Al-Cu steel							
8			about 1.2	about 2	288	388	100

Effect of Cerium on Nitrified Steel

Cerium combines with nitrogen to form CeN.[29,30] The nitride of cerium was investigated by many persons.[43,60,61] No one has tested cerium steel for nitrification. The writer tested chrome steel containing 1 to 2 per cent. cerium in the usual way but obtained no satisfactory results in chemical analyses. The results of the hardness test alone are therefore shown in Table 14.

TABLE 14.—*Tests on Chrome-cerium Steel*

Number of Steel	Chemical Analysis			Brinell Hardness		
	C, Per Cent.	Cr, Per Cent.	Ce, Per Cent.	Before Treatment	After Treatment	Difference
61	0.188	1.005	?	166	415	249
57	0.115	0.977	?	166	388	222

Analysis of Nitrogen in Iron and Steel

The writer dissolved the sample in hydrochloric acid, and then distilled it over into an excess of alkali. In order to prevent boiling and detrimental shocks, he connected all apparatus by ground-glass joints

and passed a small quantity of air free from ammonia into the boiling alkali solution (Fig. 20). A fused silica tube was used for distillation to prevent yielding alkalies in the distillate. By analyzing oft-sublimated ammonium chloride reliable results were obtained.

A Flask
B Dropping Funnel
C Condenser
D Bulb Neck
E Transparent Quartz Tube
F Erlenmeyer Flask
G Lunge's Ten-Bulb Tube
H Stopcock
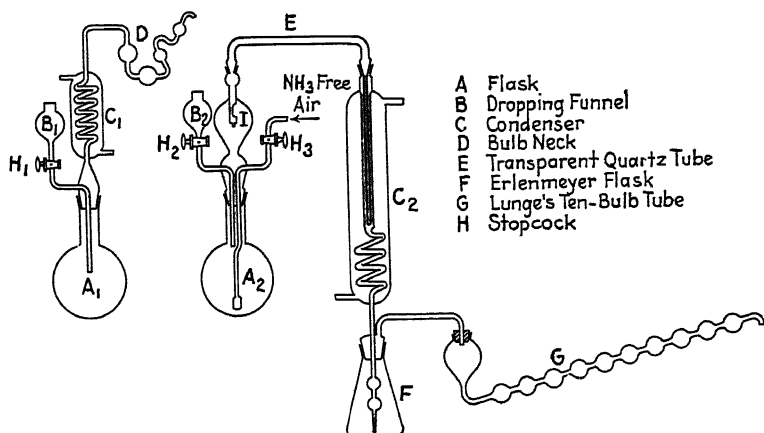
FIG. 20.—APPARATUS USED FOR ANALYSIS OF NITROGEN IN IRON AND STEEL.

BIBLIOGRAPHY

1. Siegmon: *Stahl und Eisen* (1919) **39**, 1287.
2. L. E. Benson: *Jnl.* Iron and Steel Inst. (1922) **106**, 95.
3. A. Fry: *Chem. Abst.* (1922) **16**, 1738.
4. A. Fry: *Stahl und Eisen* (1922) **42**, 1656.
5. A. Fry: German Patent No. 386510.
6. A. Fry: *Krupp. Monatshefte* (Sept., 1923) **4**, 137.
7. A. Fry: *Krupp. Monatshefte* (Dec., 1924) **5**, 266.
8. A. Fry: *Krupp. Monatshefte* (1926) **7**, 17.
9. A. Fry: *Krupp. Monatshefte* (1926) **7**, 179.
10. L. Guillet: *Compt. rend.* (1926) **182**, 903.
11. L. Guillet: *Jnl.* Iron and Steel Inst. (1927) **115**, 891.
12. L. Guillet: *Idem*, 892.
13. L. Guillet: *Compt. rend.* (1926) **183**, 933.
14. L. Guillet: *Compt. rend.* (1927) **184**, 1296.
15. A. Fry: *Krupp. Monatshefte* (Dec., 1927) **8**, 208.
16. H. Braune: *Stahl und Eisen* (1905) **25**, 1195.
17. H. Braune: *Stahl und Eisen* (1906) **26**, 1496.
18. W. Giesen: *Carnegie Schol. Mem.* (1909) **1**, 1.
19. G. S. Scott: *Jnl.* Iron and Steel Inst. (1907) **75**, 120.
20. J. H. Andrew: *Jnl.* Iron and Steel Inst. (1912) **86**, 210.
21. A. Bramley and G. H. Beeby: *Carnegie Schol. Mem.* (1926) **15**, 71.
22. L. Jordan and F. E. Swindell: *Sci. Papers* U. S. Bur. Stds. (1922–23) **18**, 498.
23. H. E. Wheeler: *Min. & Met.* (April, 1920); also *Trans.* A. I. M. E. (1922) **67**, 257; *Rev. de Mét., Extraits* (1921) **18**, 395.

24. H. B. Northrup and O. A. Knight: *Chem. & Met. Eng.* (1920) **23**, 1107.
25. N. Tschischewski: *Jnl.* Iron and Steel Inst. (1925) **92**, 47.
26. J. S. Vanick: *Metallurgist* (April, 1928) **4**, 52.
27. C. E. Ufer: *Lieb. Ann.* (1859) **112**, 281.
28. H. N. Warren: *Chem. News* (1887) **55**, 155.
29. W. Moldenhauer: Die Reaktionen des freien Stickstoffs (1920).
30. E. B. Maxted: Ammonia and the Nitrides (1921).
31. E. Baur and G. L. Voermann: *Ztsch. f. phys. Chem.* (1905) **52**, 467.
32. F. Adcock: *Jnl.* Iron and Steel Inst. (1926) **114**, 117.
33. J. Duhr: Dissertation, Aachen, 1920.
34. N. Parravano and A. Scortecci: *Chem. Abst.* (1925) **19**, 1122; *Jnl.* Iron and Steel Inst. (1925) **111**, 487.
35. J. W. Donaldson: *Carnegie Schol. Mem.* (1916) **7**, 41.
36. F. Wüst und J. Duhr: *Mitt.* Kaiser Wilhelm Inst. f. Eisen Forsch. (1921) No. 2, 39.
37. W. E. Ruder and G. R. Brophy: *Chem. & Met. Eng.* (1921) **25**, 867.
38. L. Spiegel: Braunschweig—Der Stickstoff und seine wichtigsten Verbindungen (1903) 613–17.
39. E. von Moltitz: *Stahl und Eisen* (1909) **29**, 1595.
40. N. Tschischewski: *Stahl und Eisen* (1908) **28**, 397.
41. J. Lamort: *Ferrum* (May, 1914) 225.
42. N. Tschischewski and N. Blinov: *Chem. Abst.* (1916) **10**, 2685.
43. E. Friederich and L. Sittig: *Ztsch. f. anorg u. allg. Chem.* (1925) **143**, 293.
44. F. W. Harbord and T. Twynam: *Jnl.* Iron and Steel Inst. (1896) **50**, 161.
45. P. Oberhoffer and A. Bevtell: *Stahl und Eisen* (1919) **39**, 1548.
46. H. Wolfram: Dissertation, Dresden, 1913.
47. L. Sittig: Dissertation, Berlin, 1922.
48. F. H. Hurum and Fay: *Chem. & Met. Eng.* (1922) **26**, 218.
49. C. B. Sawyer: *Trans.* A. I. M. E. (1923) **69**, 798.
50. E. Gumlich: *Stahl und Eisen* (1919) **39**, 905.
51. *Krupp. Monatshefte* (1929) **10**, 59.
52. W. Venator: *Stahl und Eisen* (1908) **28**, 1859.
53. L. Guillet: *Jnl.* Iron and Steel Inst. (1905) **67**, 743.
54. G. Mars: Die Spezialstähle (1922) 381.
55. T. P. Campbell and H. Fay: *Ind. & Eng. Chem.* (1924) **16**, 719.
56. J. K. Smith: *Stahl und Eisen* (1925) **45**, 474; *Iron Age* (1924) **114**, 1209.
57. G. Mars: *Op. cit.*, 440.
58. G. Mars: *Op. cit.*, 485.
59. *Krupp. Monatshefte* (March, 1928) **9**, 46.
60. C. Matignon: *Compt. rend.* (1900) **131**, 837.
61. W. Muthmann and K. Kraft: *Lieb. Ann.* (1902) **325**, 261.
62. *Krupp. Monatshefte* (Dec., 1927) **8**, 208.
63. *Krupp. Monatshefte* (Jan.-Feb., 1928) **9**, 23.
64. *Krupp. Monatshefte* (March, 1928) **9**, 46.
65. L. Guillet: *Le Génie Civil* (July, 1927) **91**, 38, 60, 86.
66. H. J. French and H. K. Herschman: *Trans.* Amer. Soc. Steel Treat. (1927) **12**, 921.
67. V. O. Homerberg: *Fuel & Furnace* (1928) **6**, 29, 1153.
68. H. A. De Fries: *Machinery* (1928) **31**, 478.
69. L. Guillet: *Compt. rend.* (1928) **186**, 1177.
70. G. Hägg: *Nature* (1928) **121**, 826.
71. O. Hengstenberg: *Krupp. Monatshefte* (June–July, 1928) **9**, 93.
72. A. B. Kinzel: *Trans.* Amer. Soc. Steel Treat. (1928) **14**, 249.
73. R. H. Hobrock: *Trans.* Amer. Soc. Steel Treat. (1928) **14**, 337.
74. *Krupp. Monatshefte* (March, 1928) 48.
75. *Krupp. Monatshefte* (March, 1928) 50.

Production and Some Properties of Large Iron Crystals

By N. A. Ziegler,* East Pittsburgh, Pa.

In every research it is desirable to eliminate as many variables as possible and to leave only a few to be investigated one at a time. Metallurgical problems are no exception. Some of the variables that are difficult to control are the size, the distribution, and the orientation of the grains in a metallic test piece. It is therefore very desirable to obtain isolated metallic grains (single crystals, as they are commonly called) large enough to enable one to study their mechanical and physical properties. The present investigation is a part of magnetic research work on iron and iron alloys, undertaken to obtain, if possible, the magnetic properties of pure iron (Fe). This paper will deal primarily with the preparation of single crystals of iron and their mechanical properties, while another paper, by T. D. Yensen, now in preparation, will deal specifically with their magnetic properties.

The work with "single crystals" is attracting more attention every year among the investigators in metallurgy. Van Liempt[1] gives an interesting summary of the work done and the different methods used in the preparation of metallic single crystals. Briefly stated, the four principal methods used are the following:

1. The cooling of a liquid metal in such a way that the crystallization would start at one point only, causing the entire liquid to solidify as one crystalline unit. This method can be successfully applied to the majority of the metals that do not have any allotropic transformations in the solid state. It has been used and described by a number of investigators,[2] but it has never been successfully applied to iron on account of allotropic transformations.

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[1] J. A. M. van Liempt: Production of Metallic Single Crystals. *Proc. Inst. Met. Div.*, A. I. M. E. (1928), 307.

[2] G. H. J. A. Tammann: Lehrbuch der Metallographie, Ed. 3. Leipzig, 1923. Voss. F. Stoler: *Ztsch. f. Krist.* (1925) **61**, 299.

I. V. Obreimov and L. B. Shubnikov: *Trans.* Phys. Research Lab. Leningrad (1925) **100**, 21; *Ztsch. f. Physik* (1924) **25**, 31.

J. Czochralski: Ein Neues Verfahren zur Messung der Kristallisationsgeschwindigkeit der Metalle. *Ztsch. f. phys. Chem.* (1917) **92**, 219.

S. Kaya: On the Magnetisation of Single Crystals of Cobalt. *Sci. Repts.* Tohoku Imp. Univ. [1] (1928) **17**, 1157.

H. Mark, M. Polanyi und E. Schmid: Allgemeine Beschreibung der Erscheinungen und Untersuchungamethoden. *Ztsch. f. Physik* (1923) **12**, 60.

2. Electrolytic deposition of the metal from a liquid bath on small isolated crystals of the same metal.[3]

3. Deposition of the metallic material from the gaseous state on small isolated crystals of the same metal. (Usually thin monocrystalline wire, heated by the electric current, is used.) By this method, N. Rashevsky and other experimenters have succeeded in growing crystals of tungsten and molybdenum,[4] several square millimeters in cross-section.[5]

4. Causing large grains to grow from a polycrystalline material by straining it above its elastic limit and heating to elevated temperatures. This method is the one used in the present investigation.

As early as 1898, Stead[6] pointed out that under certain conditions an abnormal grain growth may take place in steels, if they are heated to temperatures below 900° C. Later it was explained by Charpy,[7] LeChatelier[8] and Sauveur[9] that this phenomenon is due to straining the metal above its elastic limit, and annealing at a certain "critical" temperature. The critical temperature is different for every metal and alloy and for every degree of mechanical deformation. Carpenter and Elam made a valuable contribution to the science of crystal growth by working with alloys of tin and antimony and with pure aluminum.[10] O. W. Ellis was able to convert round bars of aluminum into single crystals 5 to 6 in. long and ½ in. dia. T. Sutoki,[11] by using thin strips

[3] J. A. M. van Liempt: *Op cit.* and Die Electrolytische Abschiedung des Wolframs. *Ztsch. f. Electr.* (1925) **31**, 249.

[4] F. Koref: Versuche über das Weiterwaschen von Metallkristallen durch Abscheidung aus der Gasphase. *Ztsch. f. Elektrochem.* (1922) **28**, 511.

H. Fichvoigt und F. Koref: Versuche über das Weiterwaschen von Metallkristallen durch Abscheidung aus der Gasphase. II. *Ztsch. f. Tech. Physik.* (1925) **6**, 296.

[5] Methods 1 and 2 can hardly be considered as methods for "production" of the "single crystals," because it is necessary to start with small "single crystals" obtained elsewhere.

[6] C. A. Edwards and L. B. Pfiel: Production of Large Crystals by Annealing Strained Iron. *Jnl.* Iron and Steel Inst. (1924) **109**, 129.

J. E. Stead: Crystalline Structure of Iron and Steel. *Jnl.* Iron and Steel Inst. (1898) **53**, 145.

Brittleness Produced in Soft Steel Annealing. *Ibid.* (1898) **54**, 137.

[7] S. L. Hoyt: Discussion of paper by J. A. M. van Liempt. *Proc.* Inst. Met. Div., A. I. M. E. (1928) 314.

[8] H. LeChatelier: Notes de Métallographie. *Rev. de Met. Mem.* (1911) **8**, 367.

[9] A. Sauveur: *Proc.* Intl. Assn. for Test Mats. (Sept. 3, 1912).

The Metallography and Heat Treatment of Iron and Steel, Ed. 3, 268. New York, 1926. McGraw-Hill Book Co.

[10] H. C. H. Carpenter and C. F. Elam: Crystal Growth and Recrystallisation of Metals. *Engng.* (1920) **110**, 385, 424.

The Production of Single Crystals of Aluminum and Their Tensile Properties. *Proc.* Royal Soc. (1921) **A100**, 329.

H. C. H. Carpenter: Production of Single Metallic Crystals and Some of Their Properties. *Jnl.* Iron and Steel Int. (1923) **107**, 175.

[11] T. Sutoki: On the Mechanism of Crystal Growth by Annealing. *Sci. Repts.* Tohoku Imp. Univ. [1] (1928) **17**, 857.

of aluminum, and by varying the degree of mechanical deformation, temperature and time of annealing, made some valuable observations on the mechanism of crystal growth. The most interesting conclusion he gives is that "the grain growth generally progresses from the concave side of the boundary forward," and when "the boundaries are nearly plane . . . the crystals cannot grow by any further heating." Privaut[12] gives a theoretical summary of various properties of metallic single crystals, including mechanical, magnetic, thermal, magnetostriction, etc. Gries and Esser[13] have succeeded in preparing some large single crystals of iron [strips about 6 in. (15.2 cm.) long by $\frac{3}{4}$ in. (1.9 cm.) wide], and have studied some of their mechanical properties.

However, the classical work on the preparation of the large iron crystals is by Edwards and Pfeil.[14] Since the object of the present investigation is not the study of the mechanism of grain growth but rather the study of certain properties of the single crystals, it was decided to follow the procedure of the last two investigators.

ROUND SAMPLES

It has been pointed out by almost all the investigators mentioned that foreign ingredients have a great influence on grain growth. Edwards and Pfeil[15] pointed out the interference of carbon with the growth of large crystals and Gries and Esser[16] put a particular stress on the detrimental influence of oxygen. Hence the purest iron obtainable was chosen for the material; namely, electrolytic iron, melted in the bell-jar vacuum furnace designed by Brace and Ziegler[17] and deoxidized by the addition of small amounts of carbon to the melt. The ingots thus obtained were forged into $\frac{3}{4}$-in. (1.905-cm.) round bars, and standard round tensile test pieces, $3\frac{1}{2}$-in. (8.9 cm.) effective length by $\frac{1}{2}$ in. (1.27 cm.) dia., were machined from them.

These test pieces were "normalized" in moist hydrogen atmosphere at 950° C. for 24 hr., subjected to various degrees of mechanical deformation, and reannealed in dry hydrogen atmosphere at 880° C. for 72 hr. (Fig. 1).

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[12] M. Privaut: Les Metaux Monocristallins. *Rev. Gen. des Sci.* (1928) **39**, 363.

[13] H. Gries und H. Esser: Ueber Einkristalle aus Eisen. *Archiv. f. das Eisenhütten-wesen* (1929) Group E, No. 59, **2**, 749.

[14] C. A. Edwards and L. B. Pfeil: *Op. cit.*

L. B. Pfeil: The Deformation of Iron, with Particular Reference to Single Crystals. *Carnegie Schol. Mem.*, Iron and Steel Inst. (1926) **15**, 319.

L. B. Pfeil: Effect of Cold Work on the Structure and Hardness of Single Iron Crystals and the Changes Produced by Subsequent Annealing. *Ibid.* (1927) **16**, 153.

[15] C. A. Edwards and L. B. Pfeil: *Op. cit.*

[16] H. Gries und H. Esser: *Op. cit.*

[17] P. H. Brace and N. A. Ziegler: Application of a High-vacuum Induction Furnace to the Study of Gases in Metals. *Proc. Inst. Met. Div.*, A. I. M. E. (1928) 544.

In general, the work with the round bars was a failure, because no single crystals could be prepared from them. After etching in 30 per cent. alcoholic nitric acid, sample No. V-89-11 (Figs. 1 and 3) had the appearance of a single crystal, *i. e.*, it reflected light as a crystalline unit. The sample V-89-15 showed several very large crystals. The rest of
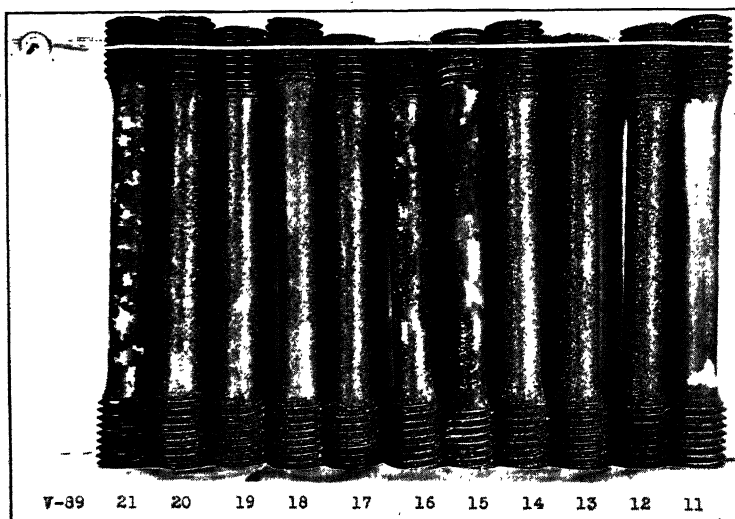
FIG. 1.—ROUND SAMPLES, ½ ACTUAL SIZE, 30 PER CENT. ALCOHOLIC HNO₃ ETCH.

the samples were more or less fine grained. However, when all the samples were cut into halves, a surprising phenomenon was discovered (Figs. 2 and 4)—all the cross-sectional areas showed very nonuniform grains. In all the samples, with the exception of V-89-11, 15 and 18, the centers are considerably coarser than the edges. Of the latter three, V-89-18 had uniform grains throughout, while V-89-11 and 15 had

FIG. 2.—CROSS-SECTIONS OF ROUND SAMPLES, ½ ACTUAL SIZE. 30 PER CENT. ALCOHOLIC KNO₃ ETCH.

fine-grained cores surrounded by a coarse-grained edge. Of particular interest is the "pseudo single crystal," V-89-11, which had an appearance of an almost perfect single crystal (Figs. 1 and 3), but actually (Figs. 2 and 4) was a shell composed of one or possibly two crystals with the inside filled with microscopic grains. The same phenomenon, not as pronounced, may be observed in sample V-89-15 (Figs. 3 and 4).
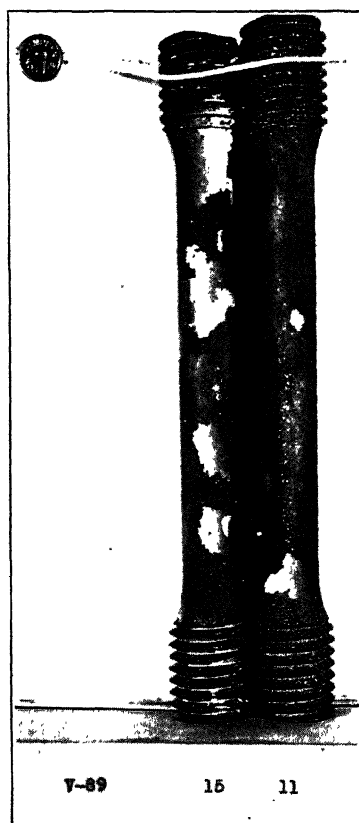
FIG. 3.—ROUND SAMPLES, ⅔ ACTUAL SIZE.
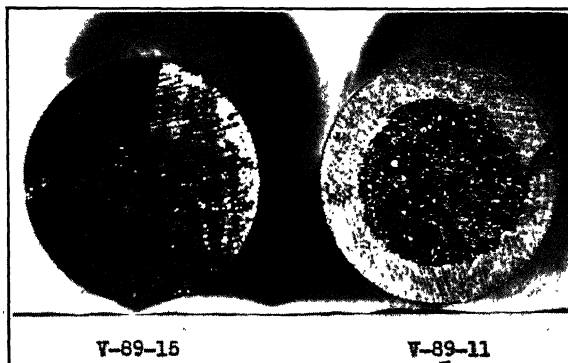
FIG. 4.—CROSS-SECTIONS OF ROUND SAMPLES, 2½ TIMES ACTUAL SIZE.   30 PER CENT.
ALCOHOLIC HNO_3 ETCH.

This observation leads to an interesting conclusion. It has been pointed out before that in order to promote abnormal grain growth for the production of single crystals, it is necessary to subject the sample to a definite mechanical deformation (within 0.25 per cent.), followed by annealing at a definite temperature (within 10° C.). As the temperature was held constant within ±5° C. during both annealing periods, the only conclusion that can be made is that the strain from the edge to the center of the bar varied at least 0.5 per cent.

FLAT SAMPLES

As it appeared, therefore, that the failure of the experiment with the round bars was due to the shape, a series of flat test pieces were machined from an Armco iron strip. Their size was 6 in. (15.2 cm.) effective length
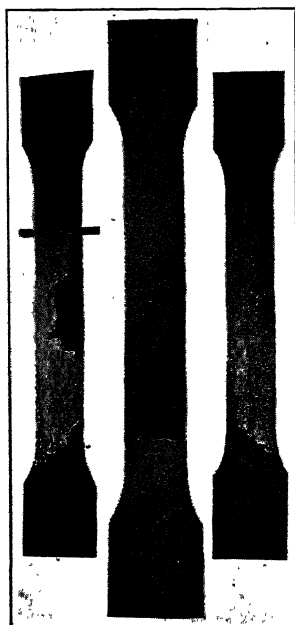
FIGS. 5–7.—ARMCO IRON SINGLE-CRYSTAL SAMPLES. 30 PER CENT. ALCOHOLIC HNO₃ ETCH.

FIG. 5.—I-61. Strained 2.25 per cent. ¼ actual size.
FIG. 6.—I-78. Strained 2.5 per cent. 0.29 actual size.
FIG. 7.—I-74. Strained 2.5 per cent. ¼ actual size.

by 1 in. (2.54 cm.) wide by ⅛ in. (0.318 cm.) thick. Each of these samples received a normalizing anneal at 950° C., a straining over the elastic limit, and a grain-growth anneal at 850° C.

There were 19 Armco iron samples; of five that were strained to 2.5 per cent. only two proved to be single crystals and of five strained to 2.25 per cent., only one became a single crystal. The other samples all
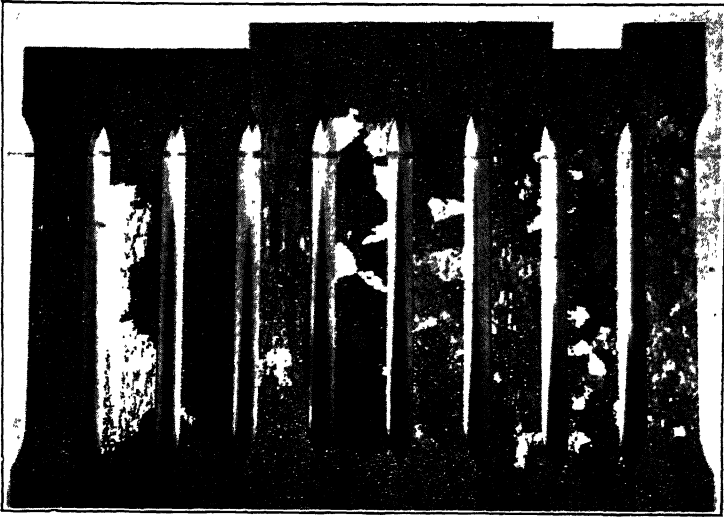
FIG. 8.—ARMCO IRON SAMPLES, ¼ ACTUAL SIZE.   30 PER CENT. ALCOHOLIC HNC₃ ETCH.

I-60.—Mostly micrograins; three macrograins.   Elong. 2%.
I-61.—Two large macrograins ("single crystal").   Elong. 2¼%.
I-62.—Mostly macrograins (3); some micrograins.   Elong. 2½%.
I-63.—26 macrograins (only).   Elong. 2¾%.
I-64.—52 macrograins (only).   Elong. 3%.
I-65.—83 macrograins (only).   Elong. 3¼%.
I-70.—Fine macrograins (only).   Elong. 3½%.
I-71.—93 macrograins (only).   Elong. 3¾%.
I-72.—Fine macrograins (only).   Elong. 4%.
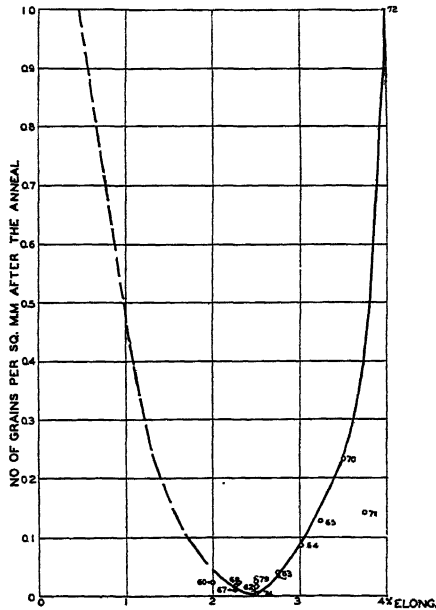
FIG. 9.—RELATIONSHIP BETWEEN PERCENTAGE DEFORMATION AND GRAIN GROWTH.

became more or less coarse grained.[18] The three single crystals are shown on the Figs. 5, 6 and 7.
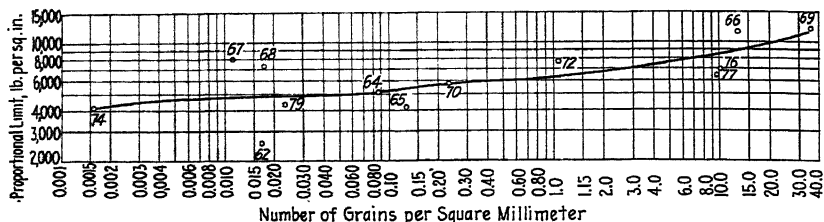
FIG. 10.—RELATIONSHIP BETWEEN GRAIN SIZE AND PROPORTIONAL LIMIT.

Some of the Armco iron samples treated as described and etched in nitric acid can be seen in Fig. 8 and all the observations that have been made are tabulated in Table 1.
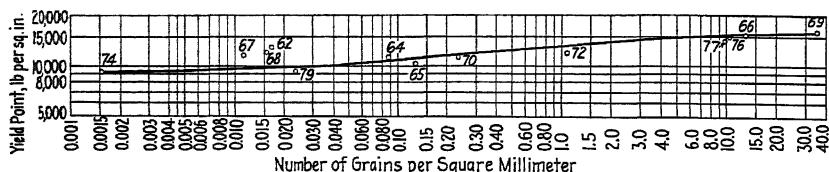
FIG. 11.—RELATIONSHIP BETWEEN GRAIN SIZE AND YIELD POINT.

The number of grains per unit area was counted for all of these samples, but in every case distinction was made between macrograins and micrograins (Table 1). Fig. 9 represents the relationship between the amount of cold work and the grain growth. It shows quite conclusively that there is a definite amount of cold work (for the given material),
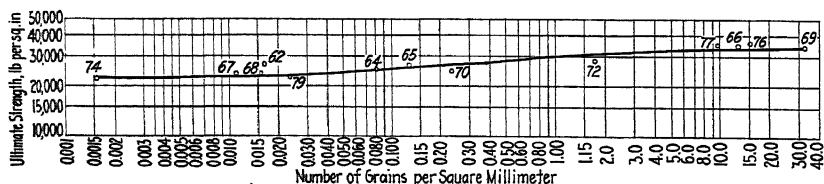
FIG. 12.—RELATIONSHIP BETWEEN GRAIN SIZE AND ULTIMATE STRENGTH.

which, followed by a suitable annealing, promotes extensive grain growth. For the given lot of Armco iron samples, this deformation is nearly 2.5 per cent. above the elastic limit.   (For other lots it may be very different, depending on chemical composition, original grain structure and other variables.)

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[18] The grains that can be counted with the naked eye are called "macrograins;" those which must be counted with the aid of a microscope are distinguished as "micrograins."

TABLE 1.—*Observations on Armco Iron Samples*

1 Serial No.	2 Original Elongation, Per Cent.	3 Total Number Macrograins	4 Mean Macrograin Area in Sq. Mm.	5 Number Macrograins per Sq. Mm.	6 Number Micrograins per Sq. Mm.	7 Proportional Limit, Lb. per Sq. In.	8 Yield Point, Lb. per Sq. In.	9 Ultimate Strength, Lb. per Sq. In.	10 Elongation in 2 In., Per Cent.	Remarks
I-60	2	3	45.2	0.022						Macrograins + micrograins.
I-61	2¼	2	?	?						Single crystal. Sent to Prof. Compton for X-ray work.
I-62	2½	8	60.6	0.0165		2,530	12,700	26,800	22.0	Macrograins + micrograins.
I-63	2¾	26	24.8	0.0403			11,300	25,000	12.5	Macrograins only.
I-64	3	52	12.4	0.0806		5,000	10,500	26,200	31.5	Macrograins only.
I-65	3¼	83	7.8	0.1282		4,100	15,400	35,900	54.0	Macrograins only.
I-66	2				12.9	11,500				Micrograins only.
I-67	2¼	2	80.6	0.0124		8,600	11,600	23,400	12.0	Macrograins + micrograins.
I-68	2¼	2	64.5	0.0155		7,300	11,200	23,900	45.0	Macrograins + micrograins.
I-69	2				35.2	11,900	16,300	35,800	64.0	Micrograins only.
I-70	3½	76	4.24	0.236		5,700	11,400	28,400	25.5	Macrograins only.
I-71	3¾	93	6.94	0.144						Macrograins only.
I-72	4	111	.93	1.075		7,650	12,000	28,500	30.0	Macrograins only.
I-73	2½	3	117.0	0.00854						Macrograins + micrograins.
I-74	2½	1	645.0	0.00155		4,300	9,300	22,100	55.5	Single crystal.
I-76	2¼				10.05	6,900	15,000	36,000	50.0	Micrograins only.
I-77	2¼				9.65	6,300	14,200	35,800	55.0	Micrograins only.
I-78	2½	1	645.0	0.00155						Single Crystal.
I-79	2½	3	43.0	0.0232		4,300	9,300	22,100	55.5	Macrograins + micrograins.

Some of these samples were pulled in the tensile test machine and the proportional limit, yield point, ultimate strength, and elongation were measured. The results of these tests are shown in Figs. 10, 11 and 12, using logarithmic scales.
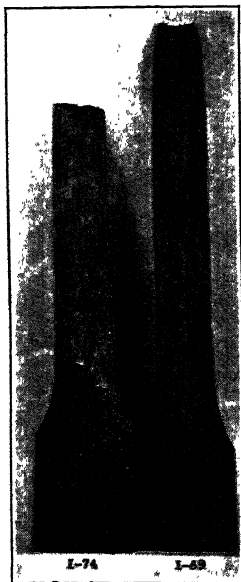
FIG. 13. — FRACTURES OF SINGLE CRYSTAL, I-74, AND OF A POLYCRYSTALLINE SAMPLE, I-69. ⅓ ACTUAL SIZE. 30 PER CENT. ALCOHOLIC HNO₃ ETCH.

All samples composed of a mixture of macrograins and micrograins inevitably fractured through the macrograins. For samples of this kind, therefore, the value of the number of grains per square millimeter was computed on the basis of the area occupied by the macrograins only, and the total number of them (Table 1, column 5). The values given in Table 1, column 6 (number of micrograins per square millimeter) were used as abscissas in cases where samples were composed of micrograins only. All three curves show increase in mechanical strength with the grain refinement, which is in accord with present conceptions. However, it is interesting to note that the values for the proportional limit and the elongation of the single crystal I-74 (Table 1, columns 7 and 10) are not the lowest and highest respectively, as might be expected. In dealing with large metallic crystals the orientation of the crystal lattice relative to the axis of the sample must be considered. This factor has a great influence on the physical properties of a crystal. (A factor which must be considered and which has not been taken into account in this series of experiments.)
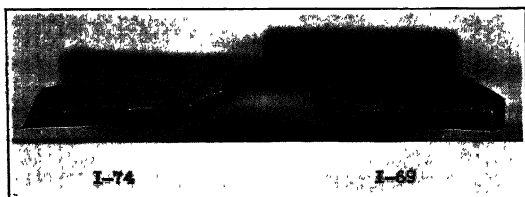
FIG. 14.—FRACTURES OF A SINGLE CRYSTAL, I-74, AND OF A POLYCRYSTALLINE SAMPLE I-69. ACTUAL SIZE.

In Figs. 13 and 14, the fractures of the single crystal I-74 and of the polycrystalline sample I-69 are represented side by side. While I-69 "necked" as usual for polycrystalline materials, I-74 pulled out to a sharp edge, diagonally across its rectangular cross-section. At the same time the whole crystal was twisted and its originally rectangular cross-section changed into a parallelogram. Figs. 15 and 16 demonstrate the

fact that when a metallic sample is mechanically deformed, each constituent grain acts as a crystalline unit, and is deformed in different directions, depending on the space lattic orientation. A very coarse crystalline (but not a single crystal) sample, I-64, which was perfectly straight before the pull, became wavy (Figs. 15 and 16, front and side) after the pull.
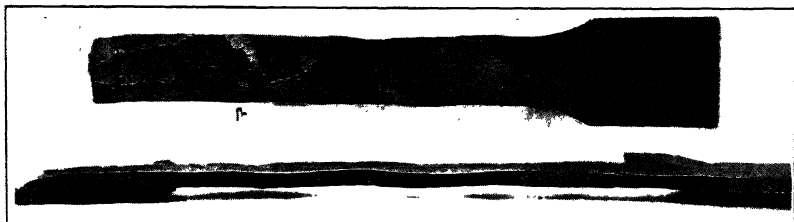
FIGS. 15 AND 16.—COARSE CRYSTALLINE SAMPLE AFTER MECHANICAL DEFORMATION. 30 PER CENT. ALCOHOLIC HNO_3 ETCH.

FIG. 15.—Front, 0.36 natural size. Crystalline boundaries are outlined with a pencil.

FIG. 16.—Side, 0.54 natural size.

Another phenomenon worth mentioning is that in all coarse-grained (but not single-crystalline) samples the grain boundaries are nearly straight lines, which is in agreement with the observations made by Sutoki[19] on aluminum crystals.
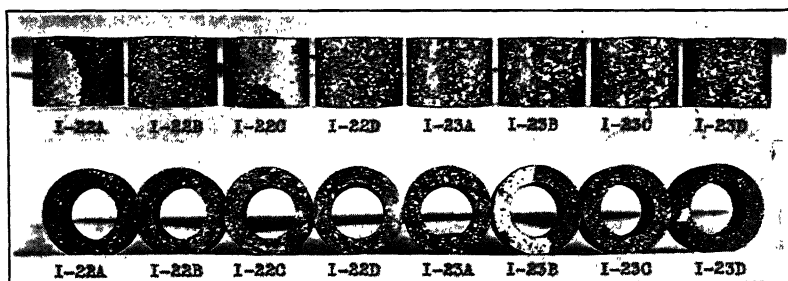
FIGS. 17 AND 18.—RING SAMPLES, 0.74 NATURAL SIZE. 30 PER CENT. ALCOHOLIC HNO_3 ETCH.

RING SAMPLES

It was desirable to study the magnetic quality of the single crystals. As straight samples are not suitable for the purpose of studying magnetic properties, it became necessary to prepare single crystals in the shape of rings. It was noticed that, in making single crystals from strips, the best results were obtained when the strips were strained 2.25 to 2.5 per cent., which corresponded to a pull of about 22,500 lb. per sq. in. (1580 kg. per sq. cm.). A series of rings, $\frac{1}{2}$ in. (1.27 cm.) high by $\frac{5}{8}$ in. (1.59

[19] T. Sutoki: *Op. cit.*

cm.) outside diameter by ⅜ in. (0.955 cm.) inside diameter, were prepared from the material that was used for the round bars. (Some of the rings were prepared from the same forgings as the round bars.) These rings were annealed in a moist hydrogen atmosphere, at 950° C. for 24 hr., subjected to various pressures from 21,000 lb. per sq. in. (1475 kg. per sq. cm.) up to 23,000 lb. per sq. in. (1618 kg. per sq. cm.) in a tensile testing machine, and reannealed at 850° C. in a dry hydrogen atmosphere for 72 hr. The magnetic permeability of every ring was tested after these treatments. Many ring samples were studied in this way. Some of the results are recorded in Table 2. Only two rings became macrogranular (I-23-B and I-23-D); the rest were all fine or coarse microgranular. Figs. 17, 18, 19 and 20 show the rings after etching.
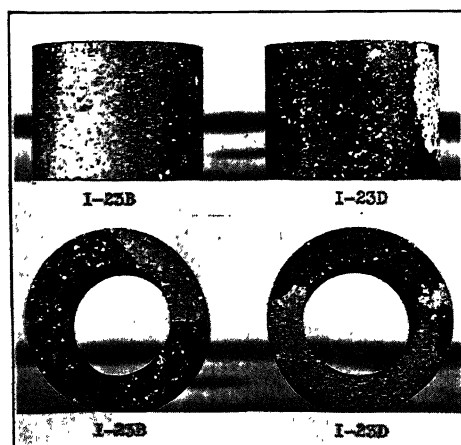
FIGS. 19 AND 20.—RING SAMPLES, APPROXIMATELY 1½ ACTUAL SIZE. 30 PER CENT. ALCOHOLIC HNO₃ ETCH.

It must be admitted that attempts to duplicate the coarse-grained rings, using the same procedure that resulted in the rings I-23-B and I-23-D, gave microgranular rings, showing that there are factors present, as yet unknown or beyond control, which retard the abnormal grain growth. To illustrate this point Fig. 21 was prepared; the points are plotted, showing the relation between the pressure applied in the preparation of the large crystals, the resultant grain size and the resultant magnetic permeability. The random distribution of the points shows clearly that some variable or variables have not been accounted for. Out of the four samples I-23-A, B, C and D, prepared from the same forging, and subjected to 22,500, 22,700, 22,900 and 23,100 lb. per sq. in. (1580, 1600, 1615 and 1650 kg. per sq. cm.) pressure respectively, numbers I-23-B and D came out macrogranular, with unusually high permeability,

while the other two turned out to be microgranular with comparatively low permeability. (See Table 2 and Figs. 18, 19, 20 and 21.)

The curves of Fig. 21 are drawn to suggest the relationships with all these variables eliminated. However, this experiment shows that
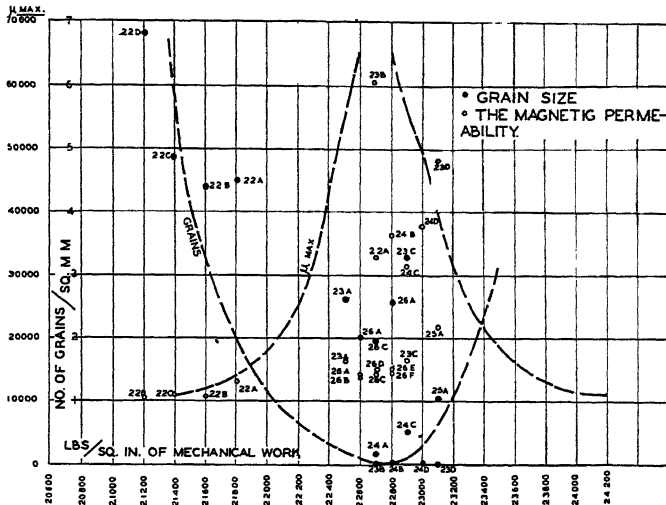
FIG. 21.—RELATIONSHIP BETWEEN AMOUNT OF MECHANICAL WORK, GRAIN SIZE AND MAGNETIC PERMEABILITY.
Curves represent ideal conditions with all other variables eliminated.

single crystals of iron can be made by the method of compression and annealing, as well as by tension and annealing, and that the magnetic quality of a single crystal is much higher than that of a polyhedral but otherwise identical sample.
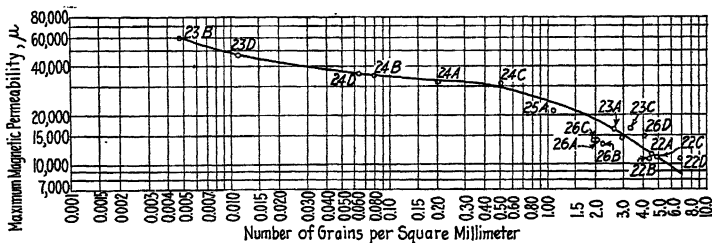
FIG. 22.—RELATIONSHIP BETWEEN GRAIN SIZE AND MAXIMUM PERMEABILITY.

The curve in Fig. 22 shows a definite relationship between the magnetic quality of iron and the grain size: the coarser the grain, the higher the magnetic quality. This is a direct confirmation of the results obtained years ago by Yensen[20] on the basis of which he concluded that a single

[20] T. D. Yensen: Magnetic and Electrical Properties of the Ternary Alloys Fe-Si-C. *Jnl.* Amer. Inst. Elec. Engrs. (1924) **43**, 558.

crystal of iron, free from foreign ingredients, must have an enormously high magnetic permeability.

Invariably it has been found that the large crystals produced either by tension or by compression were covered by fine microscopical surface crystals, usually so shallow that they could be scraped off easily with a knife. They did not interfere with the single-crystal mechanical properties of the large grains, such as the fracture, so that it is safe to assume that they have little or no effect on the properties of large crystals in general. These surface micrograins have been observed by all investigators of the production and properties of the single crystals.[21] They are probably due to the surface strains on the face of the sample, or to some sort of "unbalanced" condition of the surface layer of the atoms in a way somewhat similar to the unbalanced layer of atoms on the surface of a liquid, causing the surface-tension phenomenon.

SUMMARY AND CONCLUSIONS

1. Attempts to prepare "single crystals" of iron from round bars have failed.

2. A round-bar sample which appeared as a single crystal actually was found to be a single-crystalline shell filled with fine microscopical grains.

3. Apparently the strain across the cross-section of a tensile test piece is nonuniform, the difference being, probably, as high as several hundred pounds per square inch in a distance of $\frac{1}{4}$ inch.

4. Single crystals of iron as large as 6 in. (15 cm.) have been successfully prepared from Armco iron strips by decarburizing and normalizing the samples at 950° C. for 24 hr. in a moist hydrogen atmosphere, straining them to 2.25 and 2.5 per cent. elongation, and reannealing them at 850° C. for 72 hr. in a dry hydrogen atmosphere.

5. These results disagree somewhat with those of Edwards and Pfeil,[22] who have found that the best elongation for the production of single crystals is 3.25 per cent., followed by a 72-hr. anneal at 880° C. It is quite possible that this difference is due to a small variation in the properties of the original material, as well as in the process of preparation.

6. Single crystals possess mechanical properties, such as elastic limit, strength and ductility, very different from the polycrystalline material of the same kind. These properties are greatly affected by the orientation of the crystal lattice with respect to the axis of the pull.

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[21] S. Kaya: *Op. cit.*

C. A. Edwards and L. B. Pfeil: *Op. cit.*

H. Carpenter and Elam: *Op. cit.*

T. Sutoki: *Op. cit.*

M. Privaut: *Op. cit.*

H. Gries and H. Esser: *Op. cit.*

[22] C. A. Edwards and L. B. Pfeil: *Op. cit.*

7. Single crystals of iron have been prepared by compression (22,700 to 23,100 lb. per sq. in.), the samples otherwise heat-treated in the same way as the flat samples.

8. The magnetic permeability of a single-crystal sample is many times higher than that of a polycrystalline sample prepared from the same forging.

9. Such accidental factors as small variations in the chemical composition, the original grain size and local strains invariably interfere in the preparation of single crystals.

10. All the single crystals prepared had very small surface microcrystals, which could be scraped off with a knife and which probably have little or no effect on the physical and mechanical properties of the large crystals.

TABLE 2.—*Observations on Ring Samples*

Serial Number	Number Grains per Sq. Mm.	Maximum Magnetic Permeability	Pressure Applied in Lb. per Sq. In.	Remarks
I-22A	4.50	11,650	21,800	
22B	4.43	10,860	21,600	
22C	4.89	11,230	21,400	
22D	6.99	10,700	21,200	
23A	2.64	16,560	22,500	
23B	0.0045	60,600	22,700	Three macrograins
23C	3.31	16,560	22,900	
23D	0.01062	48,300	23,100	Seven macrograins
24A	0.1979	32,900	22,700	
24B	0.0781	36,300	22,800	
24C	0.51	31,200	22,900	
24D	0.0614	37,700	23,000	
25A	1.07	21,825	23,100	
26A	2.03	14,170	22,600	
26B	2.23	13,615	22,600	
26C	1.99	14,320	22,700	
26D	4.18	15,000	22,700	
26E	2.95	14,820	22,800	
26F	2.95	14,800	22,800	

DISCUSSION

A. V. DE FOREST, Bridgeport, Conn.—This kind of investigation seems to me the one that is going to teach us most about the mechanics of the magnetic and the general physical make-up of our iron and steel alloys. They are rather complicated in their general structures, whereas if they can be separated into single grains we can get a notion of the simple case from which there is some hope of disentangling the general properties.

Tensile Properties of Rail and Other Steels at Elevated Temperatures*

By John R. Freeman, Jr.† and G. Willard Quick,‡ Washington, D. C.

(New York Meeting, February, 1930)

THE tensile properties of steels at elevated temperatures have been studied by numerous investigators,[1] primarily for the purpose of determining their suitability for structural uses. Tests with this objective have been confined largely to the temperature range of approximately 20° to 500° C., because of the rapidly decreasing tensile strength at the latter temperature. Tests have also been extended to higher temperatures[2] for the purpose of determining the most suitable forging range. This temperature range is also of theoretical interest.

The phenomenon of increased tensile strength and decreased ductility in the so-called "blue-heat" range, approximately 200° to 300° C., is well known. It was suggested to the Bureau early in 1926 that a study of the properties of rail steels in this temperature range might prove of interest in relation to the studies of transverse-fissure failures in rails. There were available from another investigation[3] several new rails from several different heats made to approximately the same specification requirements, the complete manufacturing histories of which were known.

It was decided to determine, at least in the preliminary series of tests, only the ultimate tensile strength, elongation and reduction of area, because of the difficulty, time and cost involved in determining the proportional limit and yield point at elevated temperatures.

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* Published by permission of the Director of the Bureau of Standards.

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‡ Associate Metallurgist, U. S. Bureau of Standards.

[1] Symposium on Effect of Temperature upon the Properties of Metals. Amer. Soc. for Test. Mats. (1924) **24**, Pt. 2, 9.

[2] W. Rosenhain and J. C. W. Humfrey: The Tenacity, Deformation and Fracture of Soft Steel at High Temperatures. *Jnl.* Iron and Steel Inst. (1913) **87**, 219.

E. Dupuy: Recherches expérimentales sur les Propriétés Mécaniques des Aciers aux Températures élevées. *Rev. de Mét.* (1921) **18**, 331; also *Jnl.* Iron and Steel Inst. (1921) **104**, 91.

A. Sauveur: What is Steel? Howe Memorial Lecture. *Trans.*, A. I. M. E. (1924) **70**, 3.

T. Inokuty: Tensile Tests of Steels at High Temperatures. *Sci. Repts.* Tohoku Imperial Univ. [1] (1928) **17**, 791.

[3] J. R. Freeman, Jr., R. L. Dowdell and W. J. Berry: Endurance and Other Properties of Rail Steel. U. S. Bur. Stds. *Tech. Paper* 363 (1928) 332.

A preliminary series of tests was made on specimens from B rails from heats[4] 3, 11 and 21, the compositions, brief history and source of which are given in Table 1. This preliminary series was completed early in 1927 but in view of the unusual results obtained and their possible great importance in explaining the cause of certain types of failures, not only in rail but in other steels, it was considered desirable to withhold publication until a more detailed study could be made of the phenomenon discovered, which has been termed "secondary brittleness."

The data presented in this report are principally the results of a survey made to determine the extent to which the phenomenon exists, together with a discussion of the influence its presence in a steel may have on the final quality of the steel, and are presented with the express purpose of obtaining the helpful discussion and cooperation that comes from the publication of the results of studies of relatively little known phenomena.

TEST METHODS

The design of test specimens used is given in Fig. 1. A suitable furnace was designed and built for the purpose; it is shown schematically in Fig. 2. Two chromel-alumel thermocouples were mounted on each specimen for each test, to serve as a check on the temperature
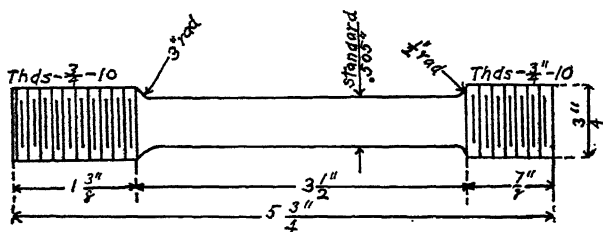
FIG. 1.—DESIGN OF TENSILE-TEST SPECIMEN USED FOR ELEVATED TEMPERATURE TESTS.

gradient in the specimen. The wires of the couples were peened into small holes drilled in the specimen at the fillets. The temperature at the middle section was estimated from a calibration in which a thermocouple was also placed at the middle section, and the temperature gradient between this section and the fillets was determined for the various temperatures at which tests were made. The temperatures of tests reported are believed accurate within $\pm 10°$ C.

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[4] Throughout this report the same heat numbers are used to designate the same material, data on which have been given in two previous publications:

J. R. Freeman, Jr., R. L. Dowdell and W. J. Berry: Endurance and Other Properties of Rail Steel. U. S. Bur. Stds. *Tech. Paper* 363.

J. R. Freeman, Jr. and H. N. Solakian: Effect of Service on Endurance Properties of Rail Steel. U. S. Bur. Stds. *Jnl. of Research* (August, 1929).

TABLE 1.—*Material Studied*

Heat No.	Chemical Composition						Remarks
	C	Mn	P	S	Si	Other Elements	
3	0.69	0.81	0.040	0.020	0.19		100-lb. B rail killed with Al, poured in sink-head ingot molds, new rail for Canadian Pacific Ry.
11	0.64	0.68	0.020	0.020	0.15		100-lb. B rail standard practice, new rail for Canadian Pacific Ry.
21	0.70	0.71	0.020	0.030	0.16		100-lb. B rail standard practice, new rail for Baltimore & Ohio R. R.
9A	0.60	0.65	0.050	0.025	0.12		¾ × 2¼-in. bar stock. Annealed. Source not known.
12A	0.98	0.39	0.024	0.019			¾ × 2¼-in. bar stock. Annealed 800° C., ½ hr., cooled slowly in furnace. Source not known.
H1C	0.73	0.60	0.026	0.050	0.25		Ladle analysis from Pennsylvania R. R.
H2C	0.74	0.63	0.024	0.070	0.31		From O position of new 130-lb. heat-treated C rail. Quenched 30 seconds.
	0.74	0.62	0.043	0.063	0.31		Ladle analysis from Pennsylvania R. R.
H3C	0.82	0.67	0.023	0.040	0.34		From O position of new 130-lb. heat-treated C rail. Quenched 15 seconds.
	0.60	0.66	0.040	0.033	0.32		Ladle analysis from Pennsylvania R. R.
M1D	0.66	1.53	0.030	0.057	0.29		From O position of new 130-lb. C rail.
	0.66	1.59	0.054	0.046	0.29		Ladle analysis.
M2D	0.59	1.21	0.022	0.045	0.21		From O position of new 130-lb. C rail.
	0.59	1.30	0.053	0.044	0.20		Ladle analysis.
CN1	0.85	0.72	0.030	0.040	0.13		100-lb. B rail failed in service because of transverse fissure. From Canadian National Ry.
CN2	0.75	0.73	0.030	0.080	0.17		From O position of 100-lb. A rail from adjoining position in track to CN1. Same service but not fissured.
PO	0.82	0.82	0.033	0.04	0.24		From O position of 130-lb. C rail failed after approximately 5 months service, because of transverse fissure. From Pennsylvania R. R.
PH1	0.68	0.79	0.021	0.020	0.16		From O position of rail from reheated bloom after service on Pennsylvania R. R.
PH2	0.52	0.74	0.023	0.020	0.16		From O position of direct rolled rail from same heat as PH1.
ST1	0.46	0.62	0.025	0.016	0.27	Cr 0.83, Mo .22	Locomotive tire steel from Standard Steel Works Co. Cooled in air.
ST2	0.44	0.62	0.028	0.017	0.27	Cr 0.83, Mo .23	Same as ST-1 but slowly cooled after forging.
E-1	0.45	1.70	0.024	0.010	0.16	Mo 0.38	Special manganese-molybdenum rail from G. N. Eaton, Molybdenum Corpn. of America.
S-17	0.62	0.73	0.047	0.050	0.15		Ladle analysis. Heat poured very hot. Rail steel.

All tests were made in a testing machine of the screw type, of 100,000 lb. capacity. A constant rate of application of stress of about 0.28 in. per minute was used in all cases except in a few special tests in which
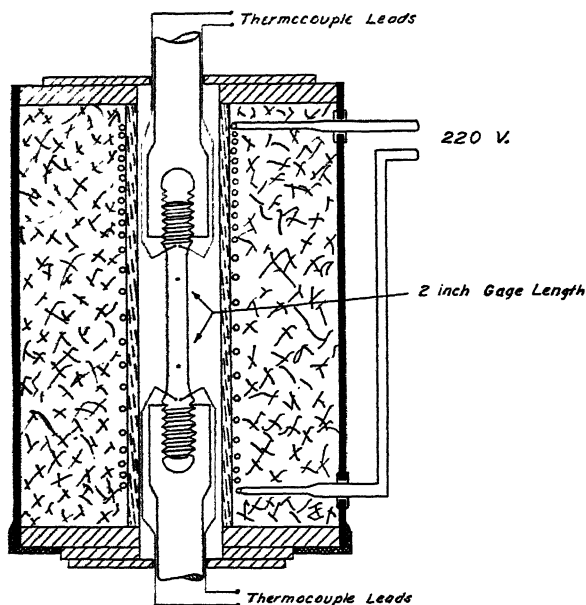
FIG. 2.—DESIGN OF FURNACE USED FOR ELEVATED TEMPERATURE TESTS.

a study was made of the effect of change of rate of application of stress on the property of the steel being investigated.

RESULTS OF PRELIMINARY TESTS ON TENSILE PROPERTIES OF RAIL STEEL AT ELEVATED TEMPERATURES

The results of tensile tests of specimens taken from the head and base of a new B rail heat 3 are given in Fig. 3. The specimens from the head of rail were taken from the *O* position and those from the base were taken at the junction of the web with the base of the rail, which has been designated the *F* position. In both cases all the specimens from each position were taken contiguously (end to end) along the length of the rail.

It is evident from the data that the tensile properties of this rail steel in the blue-heat range are characteristic of steel in this temperature range. With increase in temperature above normal (20° C.) there is first a slight drop in tensile strength followed by an increase to a maximum value at approximately 300° C. With further increase in temperature the tensile strength decreases nearly linearly with increasing temperature. The ductility values also indicate no unusual properties through the blue-heat range. There is apparently the usual slight decrease followed by a

definite increase with increase in temperature up to about 400° C. However, at this temperature a marked and unexpected inversion occurred. With further increase in temperature above 400° C. there is a marked decrease in ductility to a minimum value at approximately 650° C. The surprising fact is evident that the elongation and reduction of area of this steel at 650° C. is slightly less than at normal atmospheric temperatures. With increase in temperature above 650° C., the ductility increases rapidly to high values as the temperature of test approach is the temperature of the A₁ transformation at about 725° C.
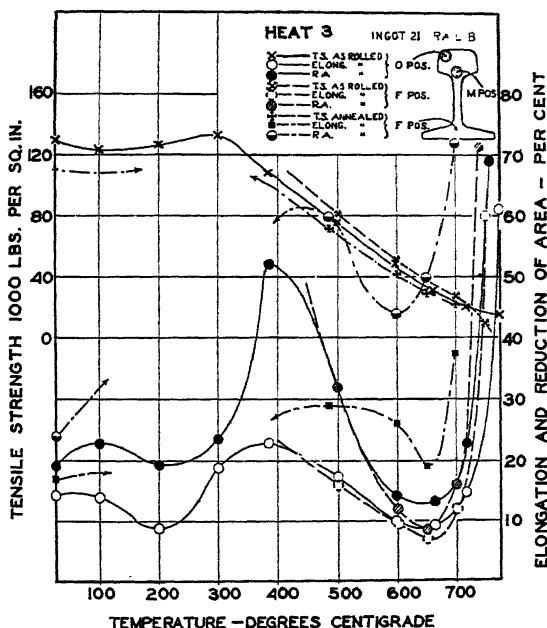
FIG. 3.—TENSILE TESTS, SPECIMENS FROM HEAD AND BASE OF B RAIL, INGOT 21, HEAT 3.

A photograph of a series of test bars after test is shown in Fig. 4. The brittle nature of the fracture is evident.

This temperature range, from 600° to 700° C., in which this rail steel showed such surprisingly low ductility, has been termed the "secondary brittle range," and the phenomenon, "secondary brittleness." It will be referred to in that way throughout this report.

Tests of specimens from the base of the rail (F position) were made to determine whether the phenomenon of secondary brittleness noted was common to the rail as a whole or possibly to an unusual segregation or allied phenomenon. The close agreement of results of tests of specimens from the base of the rail indicates quite definitely that the secondary brittleness is a property of the rail as a whole.

Similar tests were made on specimens from O position of the E rail of the same ingot and from the same position of the B rail of another ingot
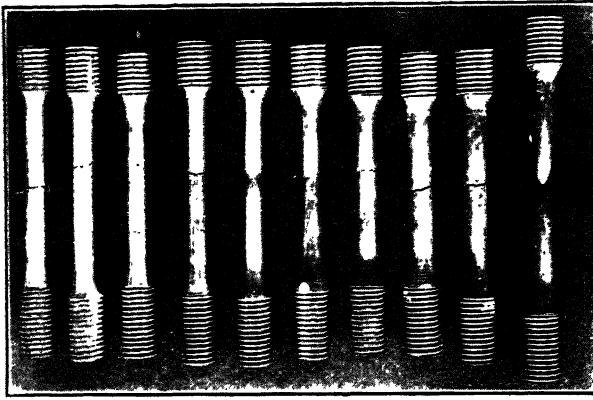
Degrees C. 20 100 200   300   400   500   600   650 700   750

FIG. 4.—TEST BARS AFTER TEST AT TEMPERATURES INDICATED.

from the same heat.   The results of these two series are given in Fig. 5. The close agreement of the results obtained indicates quite definitely
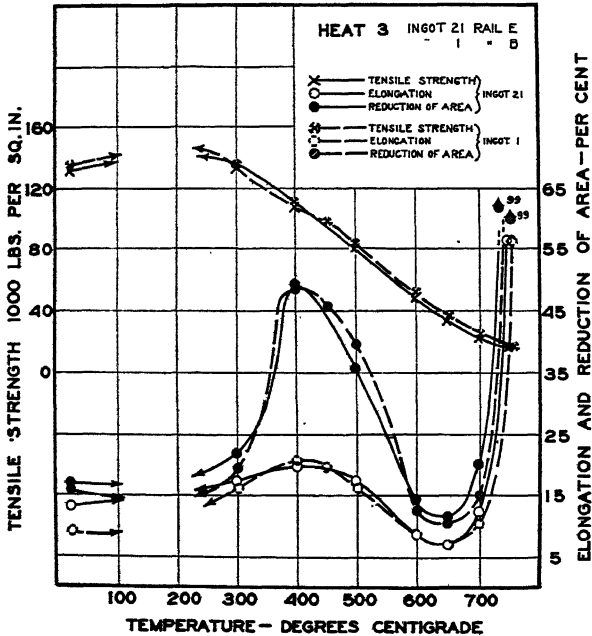
FIG. 5.—TENSILE TESTS, SPECIMENS FROM HEAD OF E RAIL, INGOT 21, AND HEAD OF B RAIL, INGOT 1, HEAT 3.

that the secondary brittleness is common to rails from near the top (B rail) and bottom (E rail) of an individual ingot, and also that it is common

to different ingots from the same heat.   Secondary brittleness appears therefore to be a property of the heat.
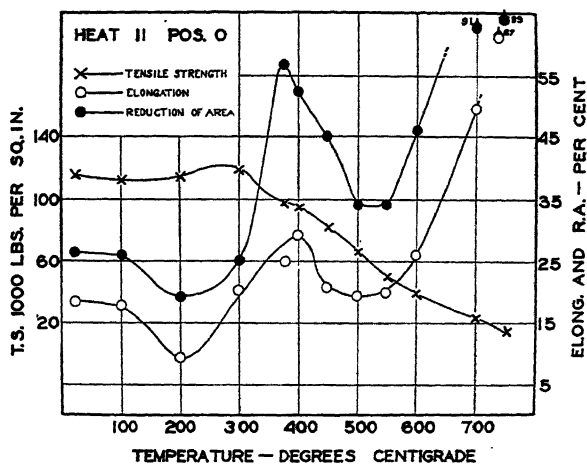
FIG. 6.—TENSILE TESTS, SPECIMENS FROM HEAD OF B RAIL, HEAT 11.

This particular heat of steel (No. 3) happened to be a special heat which had been killed with aluminum and poured into ingot molds with
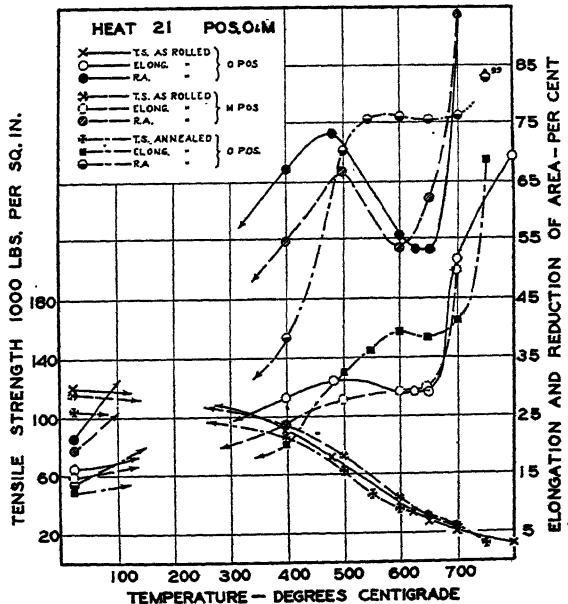
FIG. 7.—TENSILE TESTS, SPECIMENS FROM O AND M POSITIONS OF B RAIL, HEAT 21.

large end up and hot tops.   Therefore tests were made on specimens from a rail known to have been made under standard conditions (heat 11).

The results of these tests are given in Fig. 6. Secondary brittleness was evident in this material but was appreciably less marked. It is also noteworthy that the temperature range of secondary brittleness of this heat extends from approximately 400° to 600° C., with a minimum value of ductility at approximately 500° C. In heat 3 the range of marked secondary brittleness was from approximately 500° to 725° C., with minimum ductility occurring at approximately 650° C., which is appreciably higher than indicated by heat 11.

Tensile tests were then made on steel from another standard heat rolled by another steel company. The results of the tests of specimens from both the O and M positions of a B rail from this heat, No. 21, are given in Fig. 7. Secondary brittleness is indicated in this heat but to a relatively minor extent. The elongation values show only a slight drop in the secondary brittle range and the reduction of area values, while indicating a definite decrease, are at all temperatures within the range appreciably higher than the corresponding values found for the other heats.

The close agreement of the values shown by the two sets of specimens taken respectively from the O and M positions further confirm the previous indications that secondary brittleness is a property inherent to the steel.

DISCUSSION OF PRELIMINARY RESULTS

The three steels tested were from three distinct heats of rail steel made at different times and under different conditions. Heat 3 was a special experimental heat, which was killed with aluminum and poured in big-end-up ingot molds with hot tops. Heat 11 was made under standard conditions at the same plant and met the same specification requirements of the Canadian Pacific R. R. Heat 21 was also made under standard conditions, and met the specification requirements of the Baltimore and Ohio R. R. The specifications of both of these railroads are essentially the same as those adopted by the American Railway Engineering Association.

Comparison of the chemical compositions (Table 1) shows that the steels were essentially the same chemically and that all are within specification requirements. Spectroscopic analyses indicated that traces of nickel and chromium were also present but in equal amounts in all three heats. Arsenic was determined chemically and found to be 0.01 per cent. in each of the three steels.

It is evident, however, that there is a marked difference in the tensile properties of the three heats at elevated temperatures, the cause of which was not apparent.

The use of aluminum to kill the steel in heat 3 apparently was not responsible for the marked secondary low ductility, because no aluminum was used in heat 11, which showed a similar, although less marked,

secondary brittle range.   It is not known whether aluminum was added to heat 21.

In order to determine whether the low ductility noted at elevated temperatures was peculiar to rail steels, tests were made on bar stock of an approximately similar composition.   The history of this heat, No. 9A, is not known.   Its composition is given in Table 1.   The results of tests of specimens from this steel are given in Fig. 8.   No evidence of a secondary brittle range was found.   The elongation and reduction of area values increased rapidly and continuously with increasing temperature above 400° C.
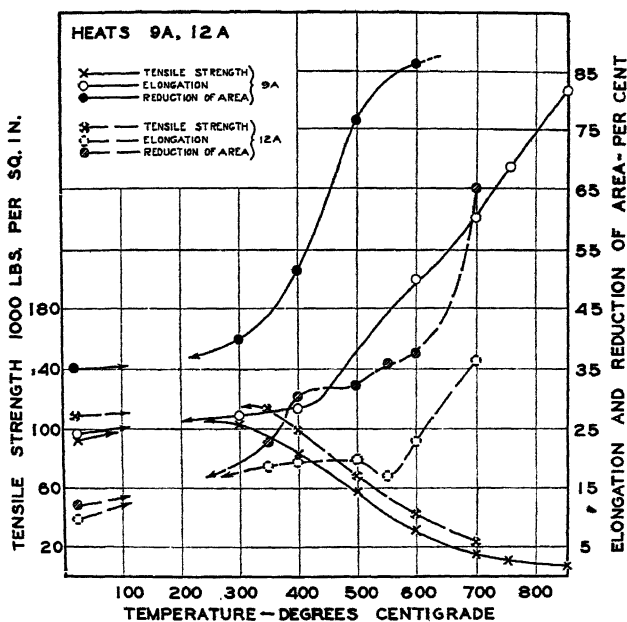
FIG. 8.—TENSILE TESTS, BAR STOCK HEAT 9A, APPROXIMATELY RAIL-STEEL COM-POSITION, AND HEAT 12A, 0.98 PER CENT. CARBON STEEL.

A search of the literature showed that the tensile properties of steels in the temperature range 500° to 700° C. had not been studied very intensively.   A review of the data of other investigators in the light of the present results brought out the fact that the secondary brittle range had been indicated and briefly referred to but its possible importance had no been appreciated or emphasized.

Welter[5] has reported on tensile properties of carbon steel with variou., manganese contents at temperatures up to 500° C.   His curves for elongation and reduction of area indicate in several instances a distinct decrease

[5] G. Welter: Elastizität und Festigkeit von Specialstählen bei hohen Temperaturen-Forschungsarbeiten a.d. *Gebeite* d. Ingenieurswesen (1921) **230**, 1.

in ductility with increase in temperature above 300° to 400° C., as is evident in Fig. 9A.

Dupuy[6] called attention to a similar inversion in the reduction of area curves for a 0.91 per cent. carbon steel, as is shown in Fig. 9B. There are indications of similar inversions in his data for the low and medium-carbon steels tested but the data were not sufficiently consistent to support definite conclusions.

In a more recent investigation[7] a very definite secondary brittle range is indicated in a cast steel. Since the present work was started evidence has been given by Inokuty[8] that secondary brittleness may be present in Armco iron although its presence was not indicated in his tests of steels of low and medium carbon. This
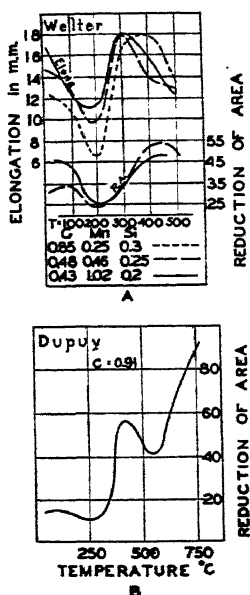
FIG. 9.—TENSILE TESTS MADE BY (A) WELTER AND (B) DUPUY.
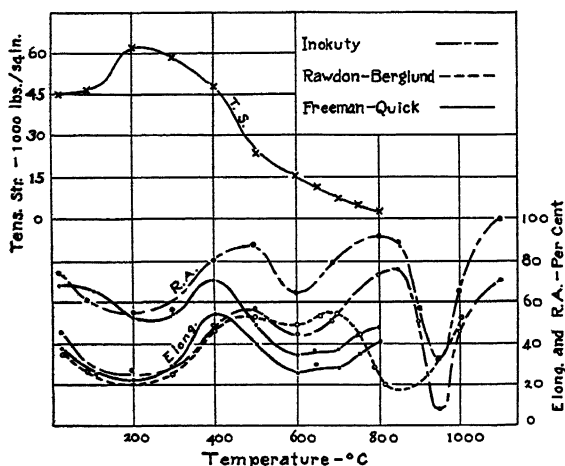
FIG. 10.—TENSILE TESTS AT ELEVATED TEMPERATURES, ARMCO IRON, BY INOKUTY, RAWDON AND BERGLUND, FREEMAN AND QUICK.

was also indicated in tests of Armco iron, by Rawdon and Berglund.[9] A definite confirmation of this was found by the authors. The results of these tests of Armco iron at elevated temperature, by Inokuty, Rawdon and Berglund and the present writers, have been plotted to the same scale in Fig. 10. The close agreement of the results obtained on a similar material in three independent investigations made at different

[6] E. Dupuy: *Op. cit.*

[7] Pioneering in Science. An Investigation of the Effect of High Temperature on Metals. Crane Company *Circular* 163, 26.

[8] T. Inokuty: Tensile Strength of Steels at High Temperatures. *Sci. Repts.*, Tohoku Imperial Univ. (July, 1928).

[9] H. S. Rawdon and T. Berglund: Unusual Features in the Microstructure of Ferrite. U. S. Bur. Stds. *Sci. Paper* 571, 698, Fig. 3b.

times is unusually positive evidence of the existence of the phenomenon. It is evident also, from the curves in Fig. 10, that what has been termed secondary brittleness is distinct from the well-known phenomenon of hot shortness in relatively pure irons which occurs at approximately 900° C. This hot-short range is shown in Fig. 10 in the curves based on Inokuty's data.

The data obtained on rail steels, bar stock of rail steel composition and Armco iron, and the similar results reported by other investigators, all indicate that secondary brittleness may be present in many steels under certain as yet unknown conditions. The desirability of a more extended study of the phenomenon was thus emphasized, especially in view of its possible relation to the presence of internal cracks, shatter cracks, in rail and other steels, as discussed fully later in this report.

TENSILE PROPERTIES OF SEVERAL RAIL STEELS AT ELEVATED . TEMPERATURES

Transverse-fissured Rails

For the studies of endurance properties previously referred to, two transverse-fissured rails[10] and a rail which had been subjected to the same identical service in track as one of them had been obtained.

One of these rails (PO) failed in track on the Pennsylvania R. R. after only about 5 months service and it had been found at their laboratories,[11] and also at the U. S. Bureau of Standards, to contain numerous shatter cracks and incipient fissures. The rail (CN1), which failed in track on the Canadian National Ry. after over 8 years service, was also shown to have contained shatter cracks and incipient fissures. In the companion rail (CN2) which had been subjected to identical service and had not failed, no shatter cracks were found.

Tensile tests were made on specimens taken from the O position in the heads of these rails. The results for rail PO are given in Fig. 11, and for rails CN1 and CN2 in Fig. 12. It is evident that secondary brittleness is present in all cases. It is particularly marked in rail PO, which showed marked internal shattering. The elongation of about 9 per cent. shown by this steel at the minimum of the secondary brittle range, which occurs at about 550° C., is practically the same as at normal temperatures. Similarly, the reduction of area of about 14 per cent. at this temperature is practically the same as exists at normal temperatures. The tensile strength, however, is only about 47 per cent. of the value obtained at normal temperature.

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[10] These are rails PO from the Pennsylvania R. R. and CN1 and CN2 from the Canadian National Ry. See footnote 4.

[11] W. C. Cushing: Rail and Wheel. *Proc.* Amer. Ry. Eng. Assn. (1929) **30**, No. 315, Pt. 1; particularly p. 268.
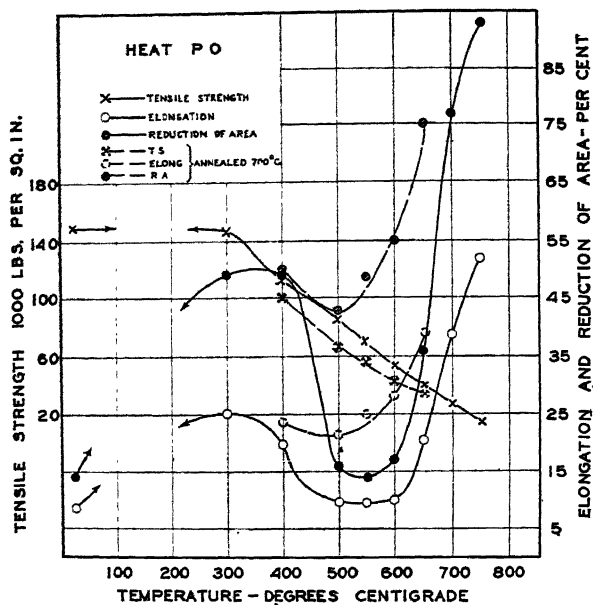
FIG. 11.—TENSILE TESTS AT ELEVATED TEMPERATURES, SPECIMENS FROM O POSITION, TRANSVERSED-FISSURED RAIL (PO) FROM PENNSYLVANIA RAILROAD.
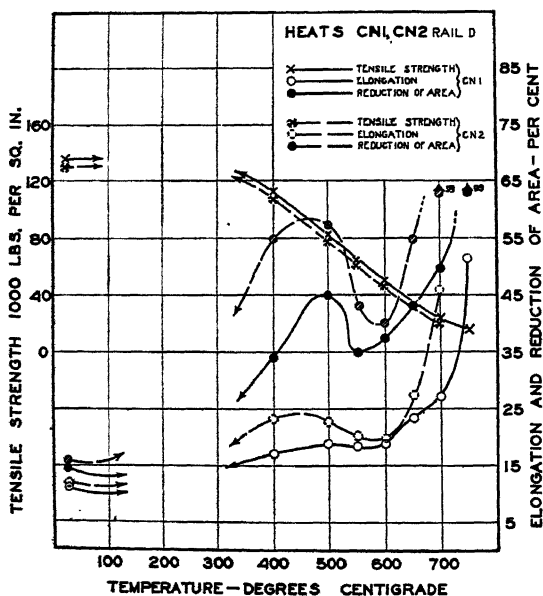
FIG. 12.—TENSILE TESTS AT ELEVATED TEMPERATURES, SPECIMENS FROM TRANS-VERSE-FISSURED RAIL (CN1) AND ADJOINING RAIL IN TRACK WHICH HAD NOT FAILED UNDER SAME SERVICE CONDITIONS ON CANADIAN NATIONAL RAILWAY.

The degree of secondary brittleness in rails CN1 and CN2 (Fig. 12) is not so marked as in rail PO, although appreciable. There is a slight difference in the tensile properties of the two steels, the steel from the fissured rail having an appreciably lower elongation and reduction of area and slightly higher tensile strength at all temperatures.

Heat-treated Rails

At the request of the Joint Rail Manufacturers Technical Committee and the Rail Committee of the American Railway Engineering Association, endurance tests have been made[12] of special heat-treated rails.
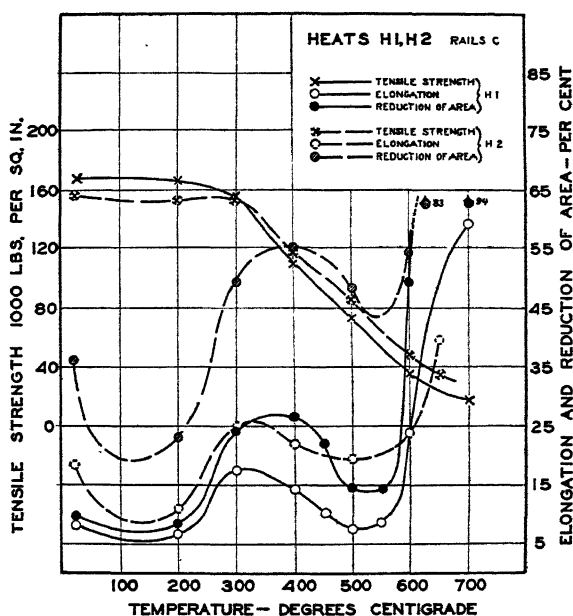
FIG. 13.—TENSILE TESTS AT ELEVATED TEMPERATURES, HEAT-TREATED RAIL STEELS.
H1C, rail quenched 30 sec. in water.
H2C, rail quenched 15 sec. in water.
Both rails after quenching held 1½ hr. in furnace at 950° F., then air-cooled.

These rails were made and heat-treated in accordance with the Kenney process.[13] The rails from one heat (H1) were quenched in water for 30 sec. The rails from the other heat (H2) were quenched for 15 sec. In each case immediately after quenching the rails were transferred to a furnace preheated to 950° F. and were held at this temperature for 1½ hr.,

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[12] To be reported soon in the U. S. Bur. Stds. *Jnl. of Research.*
[13] E. F. Kenney: Heat Treatment of Steel. U. S. Patent 1619025. Heat Treatment of Railway Rails Reissue 17240.

and were then allowed to cool in air.   Tensile tests were made on speci-
mens from the C position of the heads of a C rail, representative of each of
the conditions of heat treatments.   The results are given in Fig. 13.   It
is evident that there is a marked difference in the tensile properties of the
two steels at all temperatures of test.   It has been shown previously that
different heats of rail steel may have marked difference in secondary
brittleness.   Since these two series were from different heats, it is
impossible to state what influence the difference in heat treatment
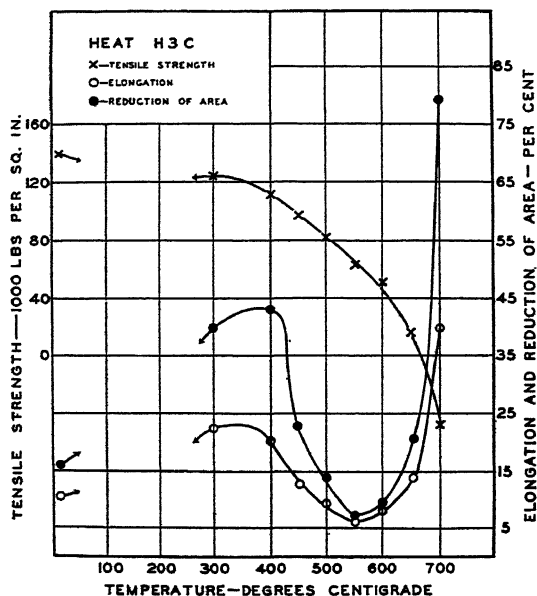
FIG. 14.—TENSILE TESTS AT ELEVATED TEMPERATURES, C RAIL, HEAT H3.

may have had on the secondary brittleness.   It is of interest, however,
to find that such a marked difference may exist, especially in reduction
of area.

Similar tests were also made on a C rail from another heat (H3) made
by the same company, which was made in the usual manner.   The results
of these tests are also given in Fig. 14.

Medium Manganese Rail Steel

The so-called medium manganese rail steels containing from 1.2 to
1.70 per cent. manganese are being used in increasing amounts.   Tensile
tests have been made at elevated temperatures, using specimens from the
O position of two D rails containing about 1.5 Mn (M1D) and 1.20 (M2D)
respectively, the compositions of which are given in Table 1.   The results
of the tensile tests are given in Fig. 15.   There is relatively slight differ-

ence in the tensile properties of these two steels at the various temperatures of test. Secondary brittleness is marked in both instances. The elongation and reduction of area values at the minimum of the secondary
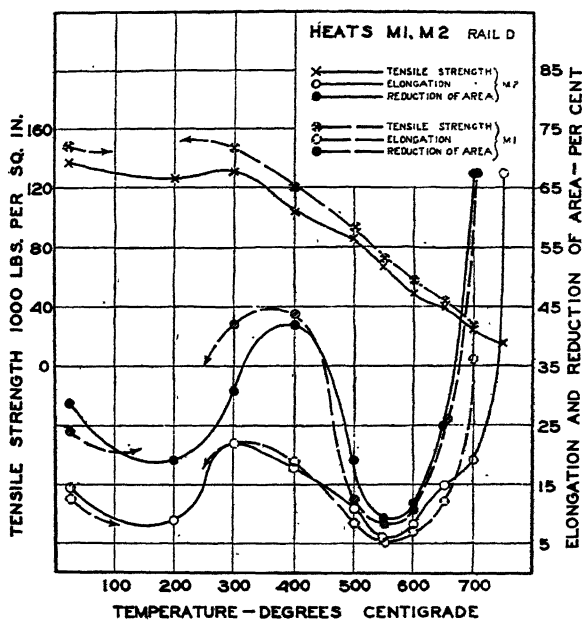
FIG. 15.—TENSILE TESTS AT ELEVATED TEMPERATURES, MEDIUM MANGANESE RAIL STEELS.
M1D, 1.5 per cent. Mn; M2D, 1.2 per cent. Mn.

brittle range, which occurs at about 550° C., are appreciably lower than at normal (20° C.) temperatures. The tensile strength at 500° C. is about 50 per cent. of the value at normal temperatures.

Manganese-molybdenum Rail

At the request of G. N. Eaton, of the Molybdenum Corpn. of America, tensile tests were made at elevated temperatures of a special manganese-molybdenum rail steel, the composition of which is given in Table 1. The results of this series of tests are given in Fig. 16. The test specimens were taken from the O position, as in the other series. Secondary brittleness is also present in this material, a minimum elongation and reduction of area occurring at approximately 600° C. It is of interest to note the relatively high values of ductility, especially of reduction of area indicated by this material at normal (20°) temperatures. The total number of tests made, one at each temperature, are rather few, so that definite

conclusions can not be drawn, and the data therefore must be considered as tentative only.
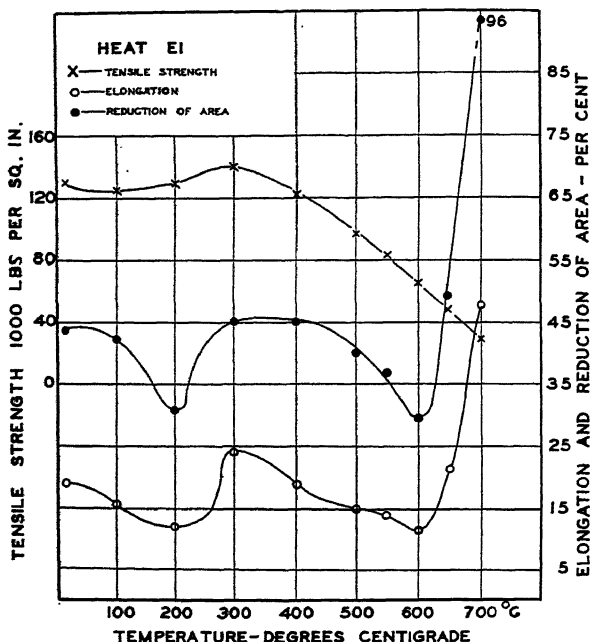
FIG. 16 —TENSILE TESTS AT ELEVATED TEMPERATURES, MANGANESE-MOLYBDENUM RAIL STEEL, HEAT E1.

Rail Steel Poured at High Temperatures

In a previous investigation,[14] data are given on the properties of a rail steel known to have been excessively hot when poured. A section of the B rail, the properties of which had been previously determined, was available, and afforded the opportunity of determining at least qualitatively whether pouring temperature had any marked influence on secondary brittleness. Results of elevated temperature tests on specimens from the O position of this rail are given in Fig. 17. Apparently a high pouring temperature has by itself no marked influence on the degree of secondary brittleness in a rail steel.

Steel from a Rail from a Reheated Bloom

In a report of studies by the Pennsylvania R. R.,[15] data are given on the relative service of direct rolled rails and rails from blooms taken

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[14] See Footnote 4.

[15] Report of Committee on Rail. *Proc. Amer. Ry. Eng. Assn.* (1927) **28**, 915; particularly Appendix B, p. 933.
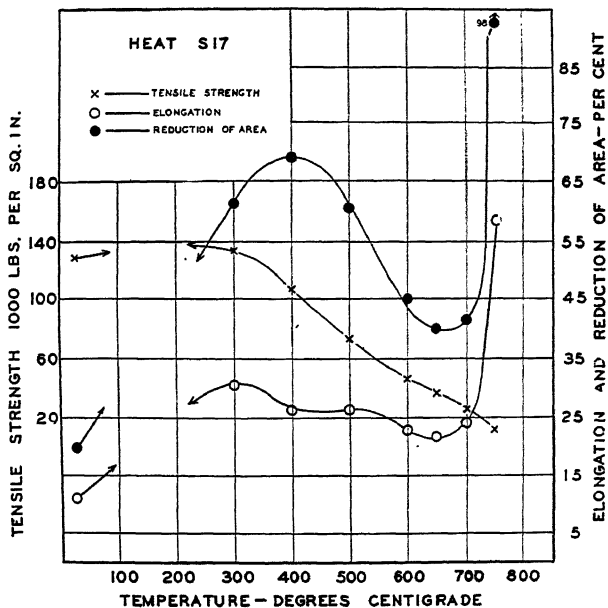
FIG. 17.—TENSILE TESTS AT ELEVATED TEMPERATURES, RAIL STEEL POURED AT HIGH
TEMPERATURE.
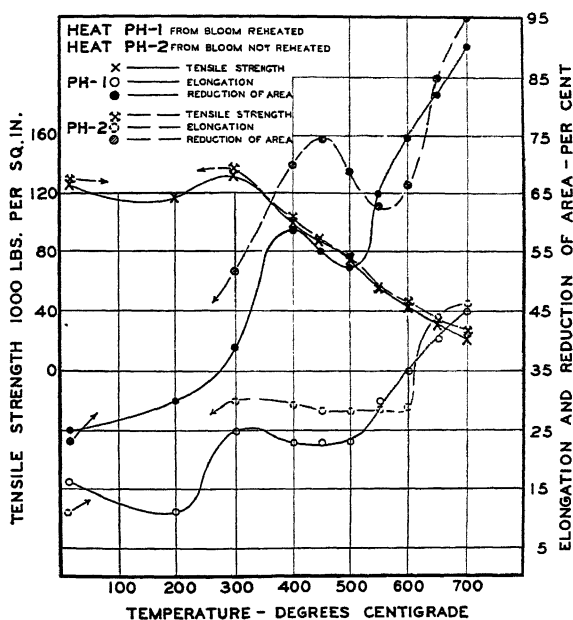
FIG. 18.—TENSILE TESTS AT ELEVATED TEMPERATURES, RAIL STEEL FROM DIRECT
ROLLED AND REHEATED BLOOMS.

PH1, reheated bloom; PH2, direct rolled bloom.

from the same heats and which had been allowed to become cold and were then reheated for rolling into rail. The service data on these rails taken over a period of several years showed that rails from reheated blooms gave better service. There were fewer failures caused by transverse fissures in these rails than in direct rolled rail. At the suggestion of Dr. M. E. McDonnell, chief chemist of the Pennsylvania R. R., tensile tests were made at elevated temperatures on specimens from two rails from the same heat, for the purpose of determining whether reheating of the bloom had caused any appreciable differences in the degree of secondary brittleness. One of these rails (PH1) was known to be from a reheated bloom and the other (PH2) from a direct rolled bloom. The results of these tests are given in Fig. 18. Both rails were from the same heat, the only known difference being the reheating of the bloom of rail PH1. Secondary brittleness is present in a relatively moderate degree in both instances. In previous work reported in this paper, it was indicated that secondary brittleness was apparently a property of the heat. Since these two rails were from the same heat it is a reasonable assumption that the difference in secondary brittleness is a result of the reheating of the bloom. Whether it is directly the result of reheating the bloom or indirectly the result of some other slight but unknown change in process, such as finishing temperature or rate of cooling, can not be stated. This is particularly noteworthy because, as shown later in this report, annealing even below the critical range has an appreciable influence on secondary brittleness. It so happens that none of the rails from this heat, either from direct rolled or reheated blooms, developed transverse fissures in track. Therefore no conclusions can be drawn regarding any possible relation of secondary brittleness to the relative freedom from transverse fissures of rail from reheated blooms.

TENSILE PROPERTIES AT ELEVATED TEMPERATURES OF SOME STEELS OTHER THAN RAIL STEELS

Chrome-molybdenum Tire Steel

In discussing secondary brittleness in rail steels and its possible relation to internal failures, as brought out more fully later in this report, it was pointed out by G. N. Eaton that certain heats of chrome-molybdenum locomotive tire steels were known at times, although infrequently, to develop cracks if allowed to cool in air from the forging temperature, but if caused to cool slowly by burying under mill scale after forging gave no such difficulty. Through the courtesy of Lawford H. Fry, metallurgical engineer, Standard Steel Works, two series of test specimens were obtained. Both series were from the same heat of steel. One series (ST1), however, was taken from a tire that was cooled in air after rolling and had developed cracks. The other series (ST2) was taken

from a similar tire which had been cooled slowly by burying in mill scale after rolling.

The results of the tests are given in Fig. 19. Secondary brittleness was present in each case but there is a marked difference in degree. The effect of the slower cooling evidently has been to decrease the magnitude of secondary brittleness. With the higher elongation and reduction of area available the steel would seem to be in a better condition to flow and so relieve any destructive thermal stresses that might be set up during
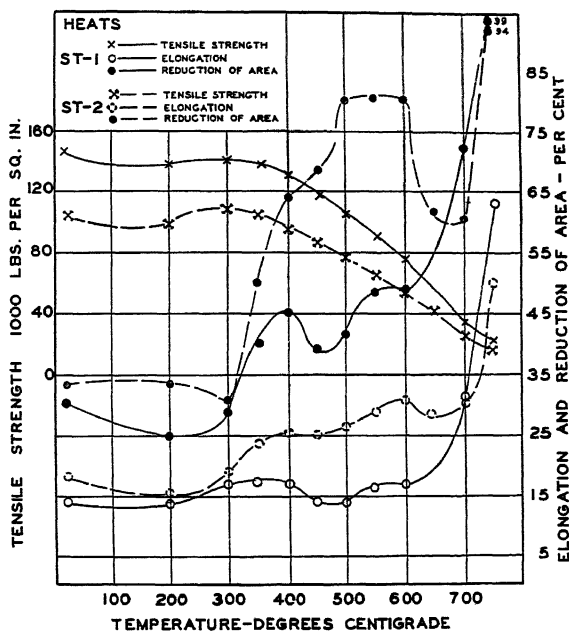
FIG. 19.—TENSILE TESTS AT ELEVATED TEMPERATURES, CHROME-MOLYBDENUM TIRE STEEL.

ST1, tire cooled from forging temperature in air.
ST2, tire cooled slowly from forging temperature by burying in mill scale.

cooling. The slower cooling would in itself greatly reduce the tendency of thermal stresses to develop and their magnitude as compared to the more rapid air cooling. The effect of the slow cooling, then, would seem to be a dual one; the magnitude of the stresses is reduced and at the same time the steel apparently is put into a condition less liable to failure should high stresses be developed. Sufficient data are not available to determine the relative importance of the two factors.

One Per Cent. Carbon Steel

It is known that free cementite is sometimes found in rail steels. In Table 1, the manganese content of the rail steels is relatively high for

steels of similar carbon content. It is known that manganese tends to shift the eutectoid ratio of carbon steels in the direction of lower carbon content. It is conceivable, with the manganese-carbon ratio present in these rail steels, that under certain conditions of segregation and rate of cooling free cementite might be present in the rail steels tested. It was thought that the secondary brittleness might be associated with its presence.

Tests were made, therefore, on a high-carbon steel (0.98 per cent. C) in which free cementite was known to be present. The history of the bar from which the specimens were taken was unknown except that before cutting off the specimens the bar was annealed so as to produce free cementite at the grain boundaries.

The results of the tensile tests are included in Fig. 8. Secondary brittleness is present in the high-carbon hypereutectoid steel (0.98 carbon) to an appreciable extent. Whether the secondary brittleness is related to the presence of the free cementite, however, can not be stated, since it was found, as is shown later in the investigation, in Armco iron and steels in which free cementite is not ordinarily present, at least in appreciable amounts. The fact that secondary brittleness was found in the annealed hypereutectoid steel is of interest and is the more significant when it is realized that the steel was in a fully annealed condition; for, as is shown later, it is known that full annealing tends to reduce markedly the degree of secondary brittleness. It may be inferred, then, that under some as yet unknown condition secondary brittleness may be marked in hypereutectoid carbon steels.

Cast Steel—0.30 Per Cent. Carbon

In some earlier work[16] secondary brittleness was indicated although not commented upon, in the ductility curves of a 0.30 per cent, carbon cast steel. A set of test bars was obtained made of such steel. This heat (DS) was made in an acid electric furnace under commercial conditions. A quantity sufficient for the number of test-bar castings desired was poured from the bull ladle into a smaller ladle, where it was recarburized with preheated washed metal. It was then poured into dry (core) sand molds. The test-bar castings were of the type shown in Fig. 20. The test specimens were all taken from the bottom portion of the casting, as indicated in the figure. The results are given in Fig. 21. Secondary brittleness is indicated to a relatively moderate degree. One specimen tested in the secondary brittle range showed very low ductility, the cause of which could not be definitely determined as being associated with cracks or blowholes or similar defects. Therefore the values obtained
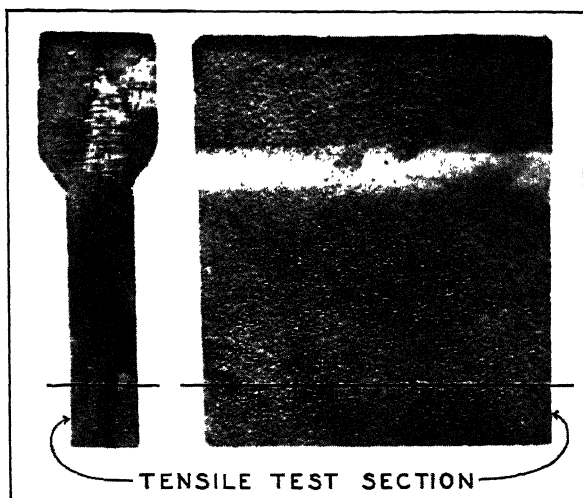
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[16] See Footnote 7.

FIG. 20.—TYPE OF CASTING USED FOR CAST-STEEL TEST BARS. ALL SPECIMENS TAKEN
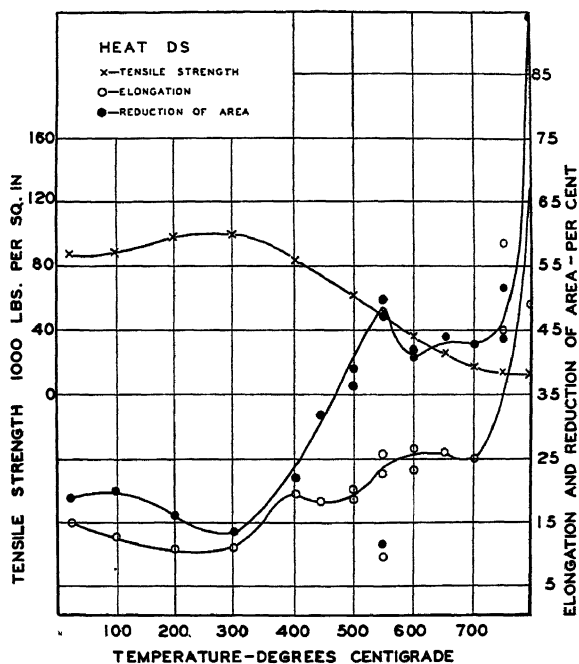FROM BOTTOM AS INDICATED.

FIG. 21 —TENSILE TESTS AT ELEVATED TEMPERATURES, 0.30 PER CENT. CARBON CAST
STEEL, HEAT DS.

are indicated in the diagram. A second specimen from a different casting did not confirm the results.

EFFECT OF RATE OF APPLICATION OF STRESS ON SECONDARY BRITTLENESS

It is well known that the values determined in tensile testing may vary appreciably with the rate of application of stress. In tests at elevated temperatures this effect is, in general, more pronounced. A rate of application of stress of about 0.28 in. per min. was used in all tests reported in this work. To determine the effect of rate of application of stress,
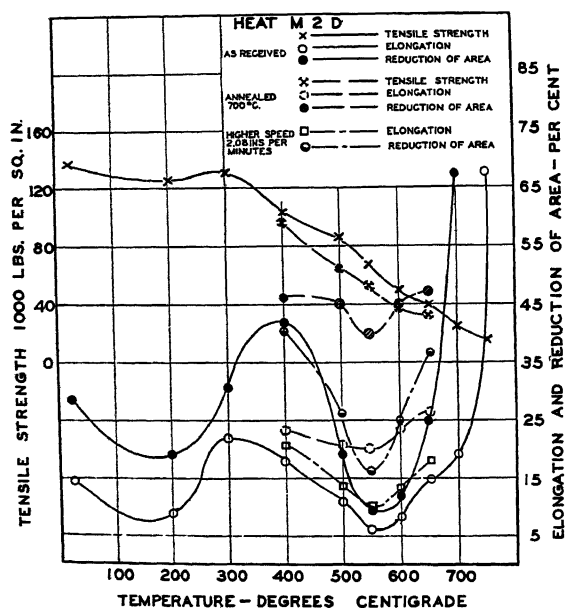
FIG. 22.—EFFECT OF ANNEALING AT 700° C. AND OF RATE OF APPLICATION OF STRESS ON SECONDARY BRITTLENESS IN MEDIUM MANGANESE RAIL STEEL.

a series of tests were made on specimens from the O position of medium manganese steel rail (M2D), using a rate of application of 2.08 in. per min. Tests were made only in the secondary brittle range. The results are given in Fig. 22. It is evident that at the higher rate of application of stress the elongation and reduction of area are slightly greater. On account of the rapid rate used it was not possible to keep the beam of the testing machine correctly balanced. Data for tensile strength at the higher speed, therefore, were not determined.

The data show definitely that secondary brittleness is not related, at least in any marked degree, to the speed of testing.

Preliminary tests were carried out to determine the effect of annealing on the secondary brittleness. A section of the B rail of heat 21, on which previous tests were made (Fig. 7), was annealed by heating at 1000° C. for 6 hr. and cooling slowly in the furnace. Tensile tests were then made in specimens from the O position. The results have been plotted in Fig. 7 for ease of comparison with the similar series of tests from the rail "as rolled." It is evident that the annealing has markedly increased the ductility in the secondary brittle range, particularly the reduction of area.

A series of specimens from the O position of the B rail from heat 3 (Fig. 3) was annealed by heating at 800° C. for ½ hr. and cooling slowly in the furnace. The results of tests of this series are included in Fig. 3. The elongation and particularly the reduction of area have been improved as a result of the annealing.

It is evident from these two series of tests made on steel from two distinctly different heats of rail steel, one of which (No. 21) was made according to standard practice and the other a special killed heat poured in hot-top ingots, that annealing the steel above the Ac transformations tends to eliminate secondary brittleness.

The effect of annealing a rail steel at a temperature above the secondary brittle range but below the A_1 transformation was then studied. A group of specimens from the O position of rail M2D was annealed by heating at 700° C. for 2 hr. and cooling slowly. The results are given in Fig. 22.

The rather surprising result is evident that heating the steel below the A_1 transformation has caused a marked decrease in the degree of secondary brittleness. As a confirmation of this a similar series of tests was made on specimens from the O position of the transverse-fissured rail PO (Fig. 11), which had been annealed by heating to 700° C. for 2 hr. and cooling slowly. The results have been included in Fig. 11.

It is evident that in this case also annealing at a temperature slightly below the Ac_1 transformation has appreciably decreased the degree of secondary brittleness.

NATURE OF FRACTURE AT ELEVATED TEMPERATURES

A photograph of a series of test bars after test at the temperatures indicated is shown in Fig. 4. The brittle nature of the fracture in the secondary brittle range is quite evident. The nature of the fracture at the several temperatures of test, whether intercrystalline or transcrystalline, was studied by microscopic means. Longitudinal sections were cut through the fractures parallel to the length of the specimens, polished and etched in the usual manner. It was not possible to study satisfactorily

the face of the fracture in most cases because of oxidation of the fractured face during the cooling down from the temperature of test. Certain characteristic features, however, were observed in the structure just back of the fracture of specimens broken in the secondary brittle range.

In the preliminary series of tests from heats 3 and 11, a distinct "intercrystalline shattering" of the metal appeared to have occurred
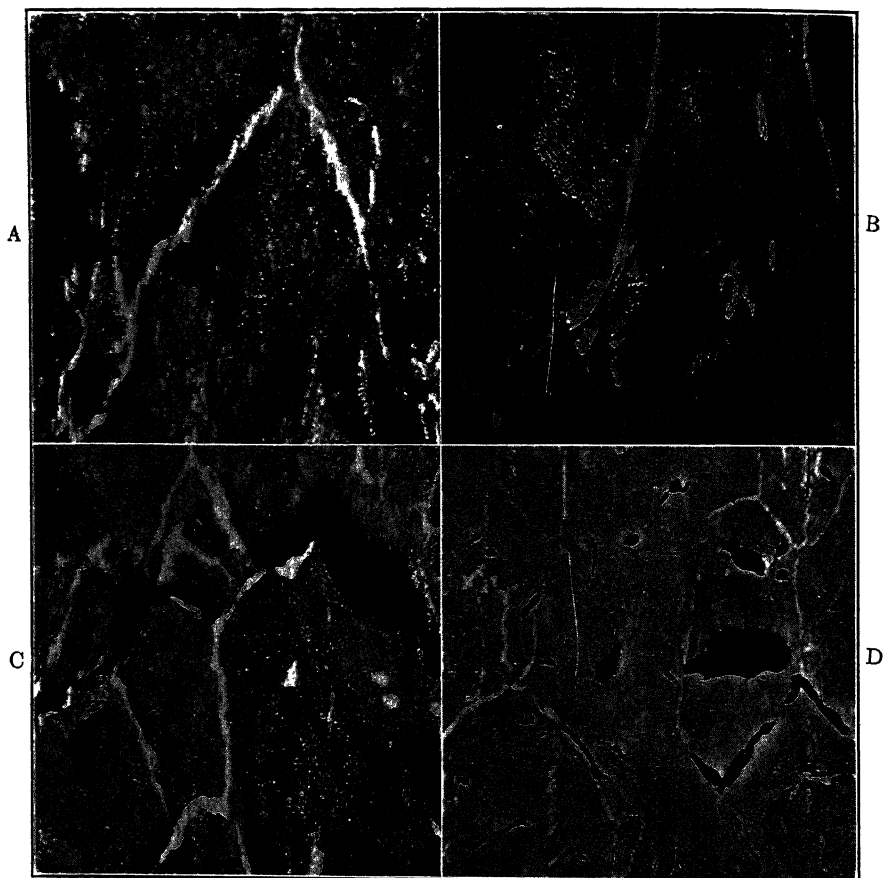

FIG. 23.—INTERCRYSTALLINE FAILURE IN TENSILE SPECIMENS FROM B RAIL, HEAT 11.
Tested at following temperatures: A, 400° C.; B, 450° C.; C, 500° C.; D, 550° C.
A, B, C etched in picric acid, × 250; D etched in hot sodium picrate, × 250.

(Fig. 23), failure occurring to a marked degree in the ferrite network or between the ferrite and pearlite at the boundary of the pearlite grains.

Fig. 24 shows a longitudinal section of a specimen from heat 3, after testing at 650° C., deep-etched in hot concentrated HCl. The general "shattered" appearance of the steel just back from the fracture is evident. A few cracks were present near the fracture of specimens

tested at all temperatures, but they were decidedly more numerous and extended farther back from the fracture in the specimens that were broken in their respective ranges of secondary brittleness.
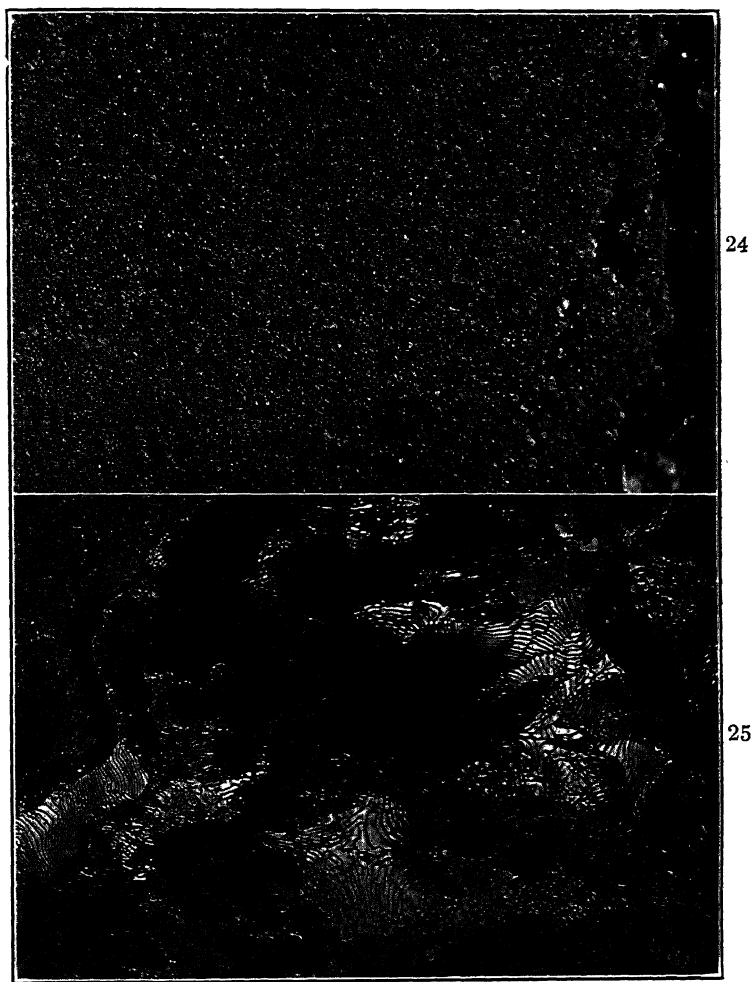
FIG. 24.—LONGITUDINAL SECTION AT FRACTURE OF TENSILE SPECIMEN, HEAT 3. Tested at 650° C., deeply etched in hot conc. HCl. × 6.
FIG. 25.—INTERCRYSTALLINE FAILURE, TENSILE SPECIMEN FROM TRANSVERSE-FISSURED RAIL PO, TESTED AT 550° C. × 500.

The same characteristic results were obtained in similar studies made of all the series of test specimens. Fracture in the secondary brittle range is characterized, in general, by a marked intercrystalline "shattering" not observed in tests at other temperatures. In heats in which secondary brittleness is not marked, such as heat 21 (Fig. 27), inter-crystalline failure was noted but to a much less marked extent.

Characteristic photomicrographs illustrative of the failure in the secondary brittle range of several of the steels tested are given in Figs. 25 to 27.   Fig. 25 shows intercrystalline failure in the secondary brittle
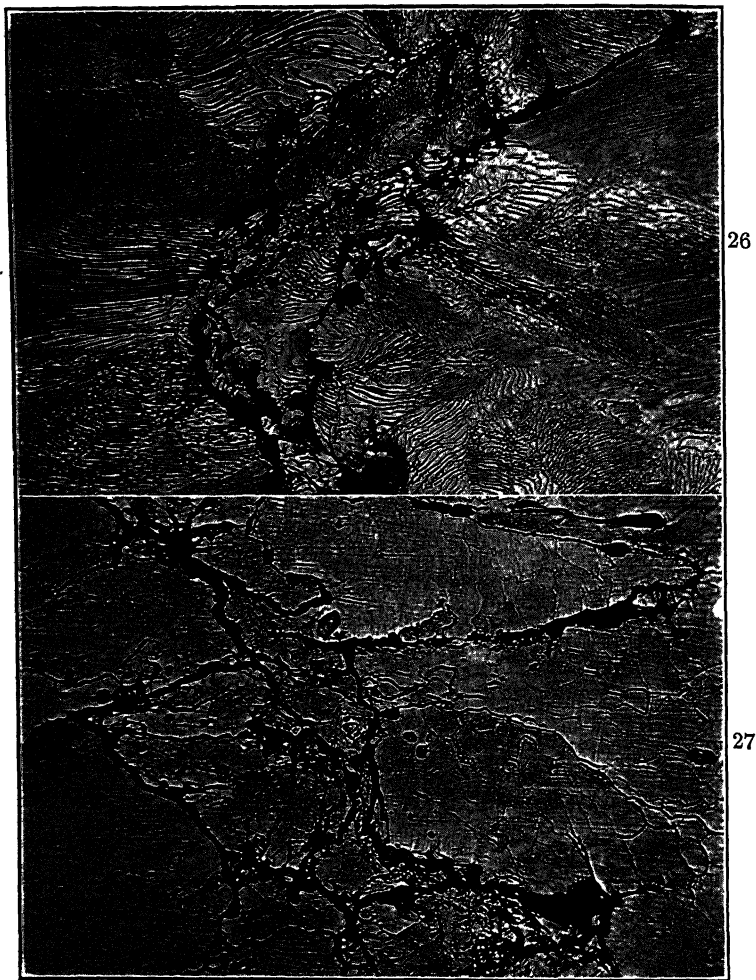
FIG. 26.—INTERCRYSTALLINE FAILURE, 0.98 PER CENT. CARBON STEEL TENSILE SPECIMEN (HEAT 12 A) TESTED AT 500° C. × 500.
FIG. 27.—INTERCRYSTALLINE FAILURE IN TENSILE SPECIMEN OF ARMCO IRON, TESTED AT 750° C. × 500.

range of a specimen from a transverse-fissured rail (heat PO, Fig. 11). In this and other fissured rails[17] intercrystalline failure had been noted in a specimen tested at normal temperatures.   There is therefore some question whether the intercrystalline cracks shown in Fig. 25 formed

[17] J. R. Freeman, Jr. and H. N. Solakian: Effect of Service on Endurance Properties of Rail Steel.   *Jnl. of Research*, U. S. Bur. Stds. (August, 1929).

during test or previously during the cooling of the rail, but there is no doubt that such failure must have occurred while the metal was hot, and it is a fact that intercrystalline failure was more marked in specimens from this rail broken in the secondary brittle range than in those tested at lower temperatures.

Figs. 26 and 27 show characteristic intercrystalline cracks in specimens of a 0.98 per cent. carbon steel and Armco iron, respectively, tested in their secondary brittle range.

The fact that intercrystalline failure is observed in the secondary brittle range of such widely diverse materials as Armco iron, rail steels and a 1 per cent. carbon steel, as well as some alloy steels, indicates definitely that secondary brittleness is not related to composition but must be related to some grain-boundary phenomenon common to all of the steels.

TEMPERATURE DISTRIBUTION IN A SECTION OF 130-LB. RAIL UNDER DIFFERENT COOLING CONDITIONS[18]

Test Methods

A rail is an unsymmetrical section. The ratio of the surface area of the base and the web to their respective volumes is appreciably greater than the ratio of surface area of the head to its volume. It follows that under similar cooling conditions the base and web of a rail would cool appreciably faster than the head. Relatively little is known regarding the magnitude of the temperature gradients that exist in a rail during cooling. Burgess and associates[19] reported the results of a few determinations made on the center and outer surface of the head of a 100-lb. rail cooled in air. The center of the head remained about 40° to 30° C. hotter than the outer surface until the critical range was approached, when the rail took on a more nearly uniform temperature throughout.

FIG. 28.—LOCATION OF THERMOCOUPLES IN RAIL SECTION FOR DETERMINING TEMPERATURE GRADIENT DURING COOLING.

A knowledge of these gradients is important. They become increasingly important in view of the experiments now being carried on by some
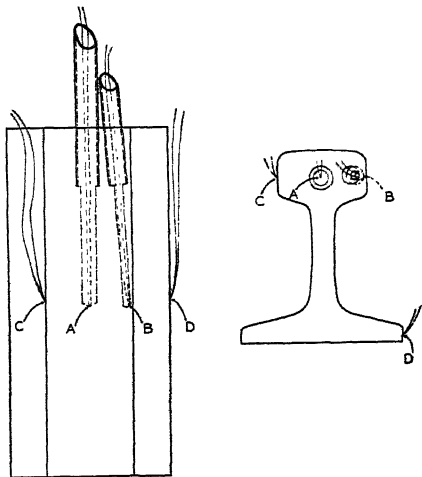
[18] The authors are indebted to T. E. Hamill, of the U. S. Bureau of Standards, for his valuable cooperation in these studies.

[19] G. K. Burgess, J. J. Crowe, H. S. Rawdon and R. G. Waltenberg: Observations on Finishing Temperatures and Properties of Rails. U. S. Bur. Stds. *Tech. Paper* 38, (1914).

of the rail manufacturers and railroads both in the United States and in Europe on quenched and tempered rails.

In some recent work at the Bureau of Standards[20] studies have been made of the surface and center cooling velocities of steel spheres and cylinders. Special apparatus was developed for these studies; it is described in the first publicati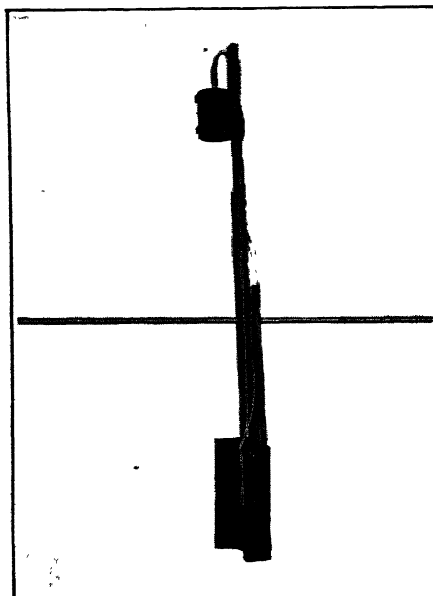on cited in the reference. The principal feature of this equipment is the use of an Einthoven string galvanometer for following the extremely rapid temperature changes of a steel surface during quenching. It is capable of recording rates of temperature change of the order of several thousand degrees a second. This same equipment has been used for determining the temperature gradients that exist in a rail under the conditions of air cooling and quenching that are reported here.

The arrangement of the thermocouples on the rail section being investigated is shown in Fig. 28. A photograph of the section with thermocouples and accessory equipment for handling is shown in Fig. 29. The thermocouples were welded to the rail at the point of contact. In the work at the Bureau of Standards on cylinders this had been found to be the most reliable method. A section of rail 12 in. long was used in all cases. Based on the earlier work on cylinders, it is believed that any error from end effects is negligible on a section of this length when the couples are placed at the midsection.

FIG. 29.—PHOTOGRAPH OF RAIL SECTION SHOWING THERMOCOUPLES ATTACHED AND FIXTURES FOR HANDLING DURING QUENCHING.

All tests were made on sections taken from a C rail of heat H3C (Table 1). In some cases, discussed later, it was necessary to use several sections due to breakage or cracking of the section in the quenching.

Five conditions of cooling were studied; namely, in still air, in moving air, quenching in cold water, interrupted quenching in cold water, and quenching in boiling water. In all cases it was possible to follow the

[20] H. J. French, and O. Z. Klopsch: Quenching Diagrams for Carbon Steels in Relation to Some Quenching Media for Heat Treatment. *Trans.* Amer. Soc. Steel Treat. (1924) **6**, 251.

    H. J. French, G. S. Cook and T. E. Hamill: Surface Cooling of Steels in Quenching. *Trans.* Amer. Soc. Steel Treat. (1929) **15**, 217.

center temperature during cooling with a portable potentiometer and to measure the time intervals with stop watches. This made it possible to follow the center cooling simultaneously with the more rapid surface cooling for which the Einthoven string galvanometer was used.

Results of Cooling in Still Air

The rail section with thermocouples attached was heated to about 900° C. and held at temperature until uniformly heated throughout. The section was then removed from the furnace and suspended vertically in air about 6 in. above the floor. All windows and doors to the room were kept closed during the entire period of the cooling of the section. The temperature-time measurements were started immediately after the section was removed from the furnace.
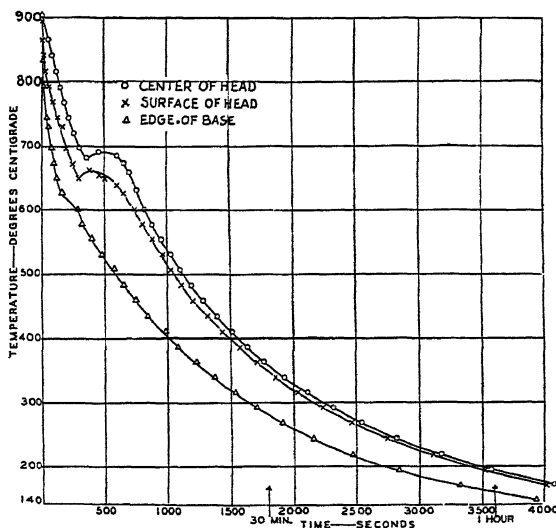
FIG. 30.—TEMPERATURE-TIME CURVES, 130-LB. RAIL SECTION, COOLING IN STILL AIR.
RUN 1.

The temperature of the center of the head, the side of the head and edge of the base were all recorded. The Einthoven string galvanometer was used to follow the temperature change on the edge of the base. Independent portable potentiometers and stop watches were used to follow the center and surface cooling of the head. The work of six operators and assistants was required to read and record the data. It was necessary to record the temperature-time changes at the three-points independently of each other. The three temperature-time curves, however, may be plotted on the same chart. Since all these curves start from the same origin of equal temperature and zero time, a direct com-

parison of the temperatures existing at any of the three points after any given period of time may be made. The results are given in Fig. 30.

It is evident that at the start the edge of the base and side of the head cool much more rapidly than the center of the head. With increasing time, the temperature difference between the edge of the base and the two points in the head increases until the edge of the base enters the transformation range, which causes an appreciable decrease in its rate of cooling. As soon, however, as the head enters the transformation range, the temperature difference between the edge of base and both surface and center of head increases very rapidly, due to the fact that the rapid rate of cooling of the edge of the base suppresses to a large extent the recalescence incident to the Ar transformations. The temperature difference between the surface and center of head is not so marked as the difference between center of head and edge of base. Following the initial rapid drop in temperature of the surface of the head to approximately 820° C., the rates of cooling of center and surface are approximately the same until the surface enters the transformation range at about 645° C., when, because the temperature of the surface is increasing while the center is continuing to cool, the surface temperature approaches the center temperature. As soon, however, as the center enters the transformation range its temperature increases, and the surface has now passed through its recalescence and is again decreasing in temperature; therefore a resultant temporary increase occurs in temperature difference between center and surface. After the center has passed through its recalescence, this temperature difference gradually decreases, with a simultaneous decreasing rate of temperature change as the rail section approaches normal temperatures.

The maximum difference in temperature between center and surface of head occurs when the surface is at about 830° C. and the center at about 895° C., almost immediately after removal of the rail from the furnace and probably at the instant a decrease in temperature first occurred in the center.

The maximum difference in temperature between the edge of the base and the surface of the head apparently occurred shortly after the latter had passed through the transformation range. At this instant, the temperature of the edge of the base was about 470° C. and the surface of the head about 610° C., a temperature difference of about 140° C. At the same instant the temperature of the center of the head was about 660° C., about 50° C. higher than the surface. The center had also just emerged from the transformation range.

The fact that a large temperature difference may exist in a rail during cooling when at these temperatures appears of significance when it is noted that the secondary brittle range in rail steels has been found to occur in the same temperature range. As discussed more fully later in

this report, the large temperature gradients existing may set up internal tensile stress, which may cause internal failure in the secondary brittle range.

Results of Cooling in Moving Air

A similar series of curves was obtained on the same rail section when cooling in moving air. In this case a current of air from an electric fan having four 8-in. blades was directed on the head of the rail during cooling. The fan was 5 ft. from the head of the rail. The results obtained are given in Fig. 31.

It is evident that the general relation of the cooling velocities of the three points to each other is approximately the same as in still air. The total time of cooling, however, is considerably less in moving air. In still air the total time required for the center of the head to cool from 900° to 200° C. was 3500 sec. while in moving air the total time required from 910° C. was only 1900 sec., or only about 54 per cent. as long. The relative cooling times of the surface of the head and edge of base were in proportion.

In still air the center cooled from 900° C. to the temperature of the Ar_3 transformation at 680° C. in 350 sec. while in the moving air it cooled from the slightly higher temperature of 910° C. to the transformation temperature in 300 seconds.

FIG. 31.—TEMPERATURE-TIME CURVES, 130-LB. RAIL SECTION, COOL-ING IN MOVING AIR. RUN 2.

There was a marked difference in the time required to cool through the transformation range at the respective positions in the rail in still air as compared to the conditions of moving air. In still air the temperature of the center remained above the temperature at which recalescence started (680° C.) for 250 sec. while in moving air the corresponding time was only 160 sec. The temperature rise, however, during recalescence was about the same (10° C.) in each instance.

The maximum temperature difference between surface and center of the head when cooling in moving air was practically the same (65° C.) as in still air and also occurred shortly after cooling first started in the center. The difference decreased but slightly until the surface entered the transformation range.
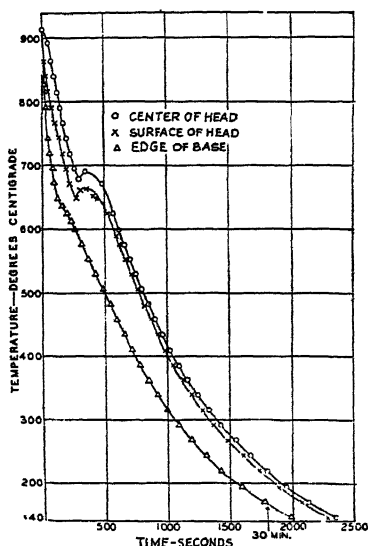
Similarly, the maximum difference in temperature between edge of base and surface of head occurred while cooling in moving air shortly after the surface of the head emerged from the transformation range, which was found under the condition of cooling in still air. The temperature difference was practically the same in each instance, being 140° C. for still air and 135° C. for moving air.

It is evident that the principal effect of the air stream from the fan flowing over the head of the rail section was to cause a more rapid cooling. The temperature distribution in the section, however, was practically the same. Any stress developed as a result of temperature gradients therefore would probably be about the same for both conditions of cooling.

Results of Quenching in Cold Water

The same section was used for this test as was used in the previous two series. It was thought that the center cooling velocity of the head would be too great to follow with the potentiometer and stop watches. Therefore in the first run of this series (No. 3) the center cooling velocity was determined, using the Einthoven string galvanometer. The section was heated to a uniform temperature of about 820° C. It was then quenched in tap water at 25° C. During quenching the section was moved up and down in the water. The temperature-time curve is given in Fig. 32 (Run 3).

A similar quench was made on this same section in which the center cooling was followed by a portable potentiometer and stop watches. The results have been included in Fig. 32 (Run 4 R) for

FIG. 32.—TEMPERATURE-TIME CURVES, CENTER OF 130-LB. RAIL SECTION, QUENCHED IN WATER. RUNS 3 AND 4.

comparison with the previous run. The initial temperature of the section, 840° C., previous to quenching was about 20° C. higher than in the previous run. The temperature of the water before quenching was 28.5° C. and after quenching had risen in the upper portion of the quenching tank to about 43° C.

The agreement of the two cooling curves is good. The greater sensitivity of the autographic string galvanometer in indicating the temperature changes is evident, particularly in showing the heat effect while passing through the transformation range.

The rail section was removed from the water when the center of the head was slightly less than 100° C. A larger crack had formed, during the quenching, at the lower end of the web and a small one was apparent on the edge of the base. When the rail was being examined, several minutes after it had been removed from the quenching water, a piece of the base broke off with appreciable force, indicating the presence in the rail after quenching of residual internal stresses of considerable magnitude. Fig. 33 shows the crack in the web, the fracture in the base and the piece that broke off. The dark area in the fracture indicates the depth of crack in the base that probably formed during quenching and acted as the nucleus for the failure that occurred after quenching. A temperature-time curve of the surface of the head was not obtained in this run, because the thermocouple broke before the end.

A similar section was prepared from an adjacent section of the same rail. Temperature-time curves for the center and surface of the head of this section during quenching are given in Fig. 34 (Run 6). The section was quenched at 850° C. into water at 25° C. The extremely rapid cooling of the surface is apparent. The total time of cooling from the quenching temperature of 850° to 300° C. was 0.6 sec. as compared to 66 sec. required for the center to cool to the same temperature.

FIG. 33.—RAIL SECTION AFTER QUENCHING IN WATER, SHOWING FRACTURE.

A duplicate run, No. 8, was made and results are included in Fig. 34. The agreement is good.

It was thought that the surface temperature of the head of the rail section, especially during the rapid cooling incident to quenching, might not be a reliable indication of the temperature a short distance beneath the surface and that the temperature in the underlying metal would more nearly approach the center temperature. Therefore cooling curves were taken simultaneously during quenching of this section, at a point
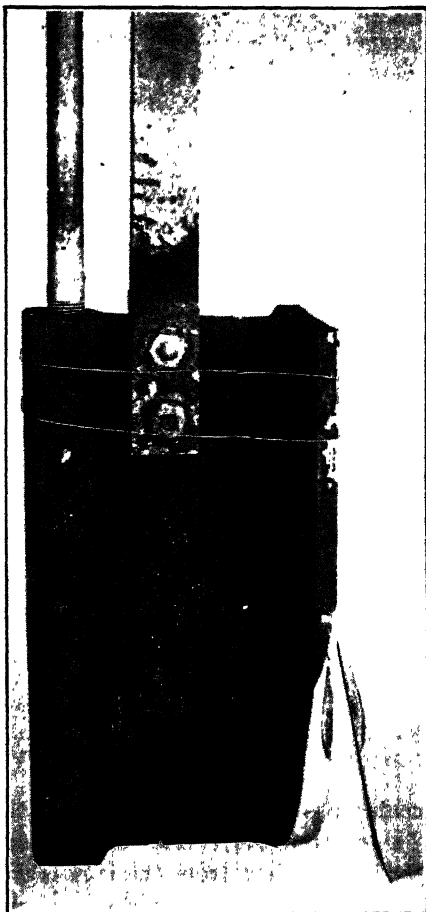
approximately ¼ in. below the surface of the head of the rail. The method of locating the junction of the thermocouple in the desired position was similar to that used for determining the center cooling, as indicated in Fig. 28. Two independent runs (7 and 9) were made. The results are included in Fig. 34.

The curves were all obtained on the same rail section. The quenching temperature was approximately the same (830° to 840° C.) in each instance. The temperature of the quenching water at instant of quenching was between 25° and 28° C. in each instance. After quenching, it was between 32° and 35° C. in the upper portion of the tank.
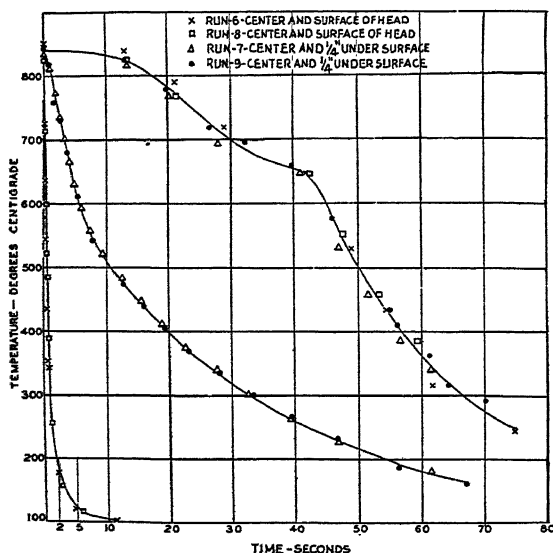
Fig. 34.—Temperature-time curves, surface, center and intermediate position in head of rail during quenching in cold water. Runs 6, 7, 8 and 9.

center cooling was followed in each of the four independent quenches. The curve is the average of the four runs.

It is evident from the curves that the surface cooling is much more rapid throughout the entire cooling range from the quenching temperature of approximately 835° to 250° C., the total time of cooling being about 0.8 sec. as compared to about 75 sec. required for the center and 43 sec. for the intermediate position.

The cooling rate at the intermediate position more nearly approximates the surface than the center cooling rate for temperatures above the transformation. The temperature at which the Ar transformations occur in the intermediate position is not well defined. A change in the rate of cooling becomes manifest, however, at approxmiately 620° C. With further decrease in temperature the cooling rate decreases rapidly. The center cooling rate is relatively slow during the first few seconds of

cooling; 11 sec. after quenching the surface temperature of the head has dropped to 100° C. while the center has decreased less than 10° C., giving an instantaneous temperature difference of over 730° C. At the same instant the intermediate position has a temperature of 490° C., or more than 340° C. below the center temperature. The occurrence of the Ar transformations is relatively well defined in the center cooling curve beginning at approximately 680° C. The rate of cooling decreases appreciably during the transformation. Immediately following the transformation the center cooling is rapid relative to the intermediate position.
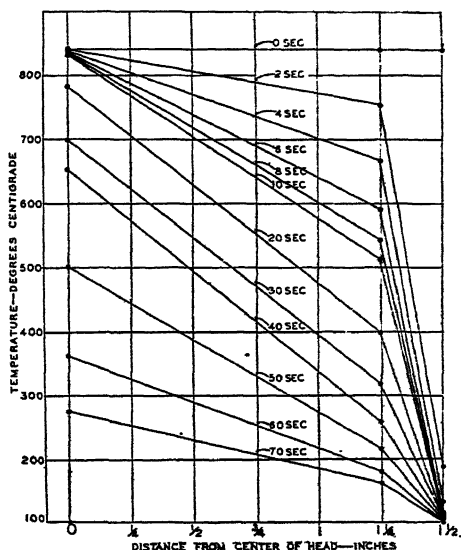
FIG. 35.—TEMPERATURE DISTRIBUTION IN HEAD OF 130-LB. RAIL SECTION DURING QUENCHING IN COLD WATER.

The approximate temperature distribution that exists in the head of the rail after certain definite intervals of time during quenching is given in Fig. 35. This plot is obtained by scaling from the curves given in Fig. 34 the temperature values at the selected time intervals and plotting them as ordinates against distance from center of rail head toward surface as abscissas. Three points only are available to indicate temperature distribution at any given time interval. These points have been connected by straight lines, although the temperature probably changes at a gradually increasing rate toward the surface. The plot indicates, however, the sharp temperature gradient that exists, especially during the first few seconds of cooling, between the surface of the head and the underlying position only ¼ in. below the surface as compared to the gradient existing between this underlying position and the center. It also indicates, as cooling progresses, the rapid increase in temperature

gradient between the position under the surface and center. The magnitude of this gradient throughout the greater part of the cooling period is also apparent.

The cooling rate of the base during quenching was not determined. In view of the fact that in air the edge of the base cooled more rapidly than the surface of the head, it would also undoubtedly cool more rapidly during quenching.

Results of Interrupted Quenching

Kenney[21] has described a special quenching procedure said to be especially applicable to rails. This process consists essentially in hardening the steel rail by quenching the rail in water to a temperature below the critical range and then before it has cooled to a temperature as low as the blue-heat zone to thoroughly equalize the temperature throughout the section, after which it may be cooled to atmospheric temperature. Kenney says that internal and external rupture occurs if the rail is allowed to cool to the blue-heat range without equalizing the temperature. That external rupture may occur is confirmed by the results obtained in the present work (Run 4) where it was found that the web and base of a short section of rail may break (Fig. 33) when quenched in water. It is also stated by Kenney that even if a rail is quenched for only 30 sec. and then allowed to cool in air, internal as well as external rupture will occur.

It was believed of interest to determine the temperature gradients in the head of a rail during an interrupted quench. Accordingly, a new section of rail was taken from the same rail adjacent to the portion from which the previous two sections were taken. The dimensions of this section and arrangement of thermocouples were the same as in the previous runs.

The section was heated to 905° C. It was then removed from the furnace and held in air above the quenching bath until the edge of the base showed magnetism as determined with a small strong hand magnet. The section was then quenched in water for 30 sec., withdrawn from the quenching bath and allowed to cool in air to normal temperatures. Temperature-time curves of the center and surface of the head were determined from the time the section was removed from the furnace until several minutes after the section was removed from the quenching bath. The results of this run, No. 10, are given in Fig. 36.

The three distinct phases of cooling are apparent: (1) cooling in air until edge of base became slightly magnetic, (2) cooling during quenching in water, (3) cooling in air after quenching. For ease of comparison, a portion of the temperature-time curves obtained on the similar section

[21] E. F. Kenney: Heat Treatment of Steel. U. S. Patent No. 1619025. Heat Treatment of Railway Rails Reissue, 17240.

during cooling in still air (Run 1, Fig. 30) have been reproduced on the larger scale of Fig. 36. As would be expected, the center and surface cooling curves of the two sections are practically the same during the initial period of air cooling. Judging from the temperature-time curve of the edge of the base obtained in the previous run, appreciable magnetism appeared when the temperature of the edge of the base was at approximately 645° C. (Judging from color, the temperature of this surface was considerably less.) The temperatures of the center and surface of the section were, at the moment of quenching, 810° C. and 740° C., respectively. The extremely rapid rate of cooling of the surface of the
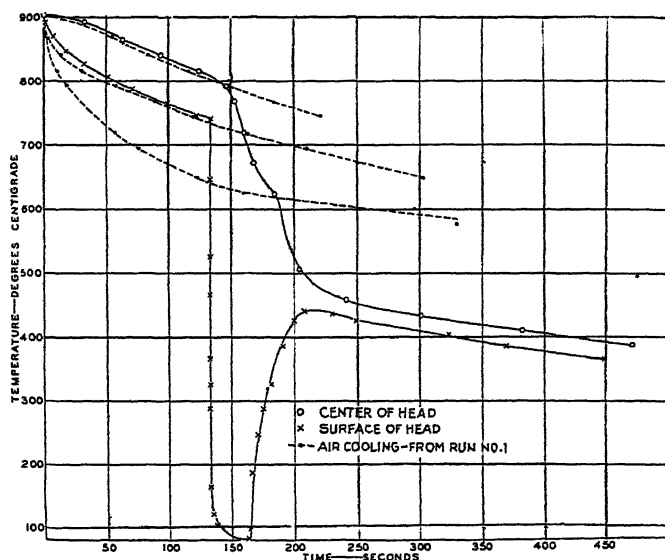
FIG. 36.—TEMPERATURE-TIME CURVES, 130-LB. RAIL SECTION DURING INTERRUPTED QUENCHING IN WATER. RUN 10.

head during quenching is apparent and is comparable to that obtained in the previous runs. The surface temperature cools from 740° to 200° C. in less than 1 sec. There is no marked change in the rate until about 120° C. is reached. During the remaining period of the quench, about 28 sec., the surface temperature cools to a minimum of 82° C. On removal from the quenching bath the surface temperature rises rapidly, attaining a maximum temperature of 444° C. in 45 sec., and then again decreases continuously at a relatively slow rate.

During the 30 sec. that the rail section was in the quenching water the center temperature decreased from 810° C. to about 700° C. and, it is of interest to note, had apparently not entered the Ar_3 transformation range. During the period that the surface temperature was rapidly increasing after removal from the quenching water the center temperature continued

to decrease rapidly through the Ar transformation range, the central portion of the head giving up its heat to the cooler exterior. At about 470° C. a condition of equilibrium appears to be established and center and surface cool at about the same rate with a temperature difference of approximately 25° C.

Equipment was not readily available for equalizing the temperature of the section after quenching by transferring back into a furnace at approximately 510° C. (950° F.), as recommended by Kenney, and thereby having the temperature equalized throughout the section. Had this been done it is obvious from the results given in Fig. 36 that the surface temperature would have increased after quenching at a somewhat more rapid rate. It is difficult to estimate the effect on the center cooling. It would seem to depend largely upon the time required to transfer the section from the quenching bath into the furnace. If this were done instantaneously the rate of cooling of the center through the transformation range might, due to a more rapid rise in surface temperature, be appreciably decreased. If 15 sec. were required to complete the transfer, the center, as may be seen from the curves, would already have passed through the transformation. Had the section been quenched for a shorter period of time, for example 15 sec., the rate of cooling of the center through the transformation range would apparently have been appreciably slower, even with air cooling of the section after quenching, and if the section were reheated after quenching the rate would conceivably have been so slow as not to produce appreciable hardening. This indicates quite definitely that a rather critical relation exists between time in quenching bath, time required to transfer from quenching bath to a reheating (equalizing) furnace and resultant hardness of the center of the head of the rail.

Results of Quenching in Boiling Water

A somewhat less drastic quench than in cold water would be desirable for rails in order to eliminate the excessive temperature gradients and the accompanying stresses. Oil might be suitable as a quenching medium but because of the large volume required and difficulties of handling as well as cost would probably not be feasible for treating a tonnage production such as rails.

It is a well-known fact that the rate of cooling of a steel object is considerably slower in hot water than in cold water. In a recent report[22] it was shown that water at 60° C. gives a cooling rate intermediate between oil and water, and might be suitable, but the difficulties of

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[22] H. J. French and T. E. Hamill: Hot Aqueous Solutions for the Quenching of Steels. Amer. Soc. Steel Treat. Preprint 8 (1929).

maintaining at a prescribed temperature the large volume of water that would be required in the production of rails would be difficult. In the same report boiling water is not considered so desirable a quenching medium as some others. It does give, however, an intermediate cooling rate between air at 20° C. and oil at 20° C. and it would be relatively easy to maintain its temperature at or very near the boiling point in the mill.

It was believed of sufficient interest, therefore, to determine the center and surface cooling speeds of a rail section when quenched in boiling water. Two runs (11 and 12) were made in which a section similar to that used in the intermediate quenching experiments was quenched in boiling water. The results are given in Fig. 37. The temperature of quenching was about 835° C.

It is evident from the curve that the cooling rate, especially of the surface, is much less than in water at 20° C. but appreciably faster than in air. The Ar transformation is evident in the surface temperature-time curve as well as in the center curve. The rate of cooling of the latter, however, was relatively so slow that it appeared questionable whether any worth-while increase in hardness

FIG. 37.—TEMPERATURE-TIME CURVES, 130-LB. RAIL SECTION DURING QUENCHING IN BOILING WATER. RUN 12.

would be obtained as compared to present practice. A section was cut from the middle portion of the quenched section; the hardness is given in Table 2, in which hardness previous to quenching is also given for comparison. Apparently some increase in hardness was obtained by reheating and quenching in boiling water. Further tests must be made, however, before definite conclusions may be drawn. It should also be pointed out that the reheating and quenching incident to the experiment would probably give higher values than would be obtained by quenching directly after rolling.
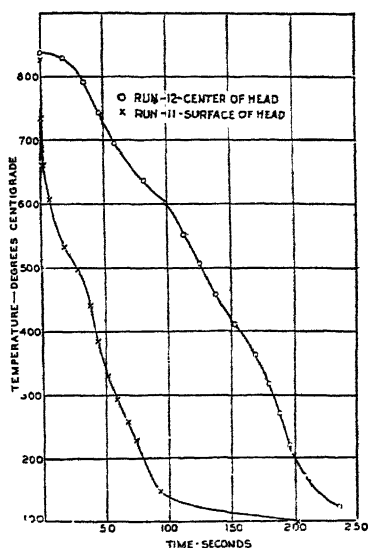
TABLE 2.—*Hardness of Middle Portion of Quenched Section*

	Rockwell B Position		Brinell 3000-kg. Load Position	
	O	M	O	M
Rail H3C as rolled..................	103	103	285	285
Rail H3C quenched in boiling water..	107	107	341	321

DISCUSSION OF RESULTS WITH SPECIAL REFERENCE TO SHATTER
CRACKS IN RAIL

Waring and Hoffammann[23] have shown the presence of internal cracks
in both new and failed rails and forgings and suggested that these cracks
might be the nucleus from which transverse-fissure failures in rails develop.
The cracks were found to be both intercrystalline and transcrystalline in
character and were believed by the authors to develop during some stage
in the process of fabrication of the material.

Howard, in his discussion of their paper, says that the cracks probably
occur when the steel is at a fairly high temperature. He pointed out in
this and in a later report[24] that internal strains of tension develop in cast,
rolled or forged shapes on cooling, that this tensile stress may be along each
of its three axes, that the shattering may be related to the rate of cooling
and that shrinkage cracks represent the relief of the strains by reason of the
rupture of the metal. It has been stated[25] that the shattered zones found
in rails do not extend to the ends of the rail, indicating that the time of
occurrence is after the rail length is cut at the hot saw.

Fig. 38 shows the thermal expansion and contraction curves of a steel
of rail-steel composition; the steel contracts on cooling at an approximately
uniform rate to 685° C., where a marked expansion occurs. With further
cooling the steel again contracts at an approximately uniform rate until
normal temperatures are reached. This dilation of steel is a well-known
phenomenon; it is associated with the transformation of gamma iron to
alpha iron. It will occur in all rails of normal composition, the temperature
depending principally on the carbon and manganese content and the rate
of cooling.

Consider the cooling of a rail after leaving the hot saw. The rail is
generally given a predetermined camber with the head convex, this having a
radius of curvature which experience has shown will cause the rail to be
approximately straight when cold. The rail is then placed on the hot bed
and starts to cool with its head convex. Figs. 30 and 31 show that as a
rail section cools in air the base cools more rapidly than the head. Accord-
ing to Fig. 38, the base will contract more rapidly than the head. This
contraction acts to increase the camber originally placed in the rail. The
contraction is resisted by the rigidity of the head and so exerts a tensile

[23] F. M. Waring and K. E. Hoffammann: Deep Etching of Rails and Forgings.
Proc. Amer. Soc. Test. Mats. (1919) **19**, Pt. II, 182.

[24] Interstate Commerce Commission Report of the Director of the Bureau of
Safety in Regard to Investigation of an Accident Which Occurred on the St. Louis-
San Francisco Railway Near Victoria, Miss., on Oct. 27, 1925 (June 16, 1927).

[25] M. H. Wickhorst: The Relation of Shattered Steel in Fissured Rails to the Mill
End of the Rail. *Proc.* Amer. Ry. Eng. Assn. (1921) **22**, 216.

J. E. Howard: On Shattered Zones in Certain Steel Rails. *Proc.* Amer. Soc.
Test. Mats. (1920) **20**, Pt. 2, 44.

stress on the head, at least in its top surface, causing a resultant tensile stress to be set up in the base.   However, because of the low strength and plastic nature of steel at temperatures above the A_3 transformation, the stresses developed are probably very small.

According to Fig. 30, the base enters the transformation range before the head and, according to Fig. 38, expansion then occurs.   This acts to relieve any tension that may be present in the base and consequently in the head.   The transformation on the surface of the head occurs somewhat
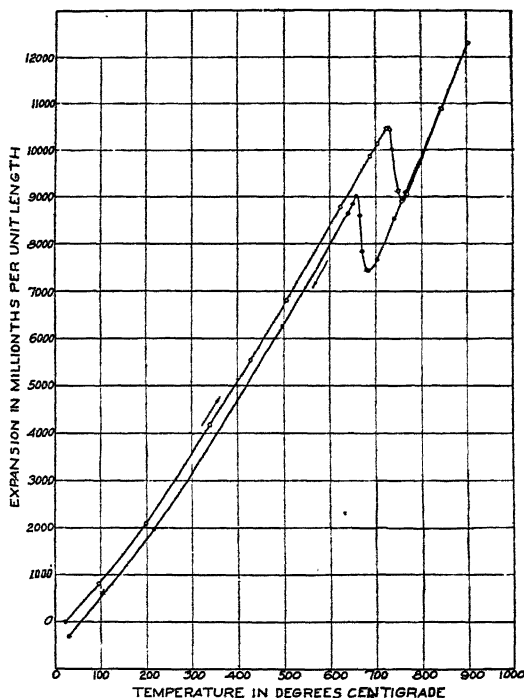
FIG. 38.—THERMAL EXPANSION CURVE OF STEEL OF RAIL COMPOSITION.
C, 0.59; P, 0.024; Mn, 0.92; S, 0.033; Si, 0.25.
(U. S. Bur. Stds. S. P. No. 433)

later than on the edge of the base (Fig. 30).   It appears probable, therefore, that the base being of lighter section passes completely through the transformation range before marked expansion will occur in the head.   If this be true, the base will be contracting while the head is expanding incident to its cooling through the transformation range.   The expansion of the head will tend to compensate for the contraction of the base and so tend to prevent the developing of internal stresses.   However, as soon as the head emerges from the transformation range, cooling of the head is relatively rapid; the head, in fact, as is evident in Figs. 30 and 31, cooling more rapidly than the base.   The more rapid rate of cooling is accompanied by a more

rapid contraction. This relatively high rate of contraction is resisted by the slower contracting web and base, which must simultaneously develop a tensile stress in the head and which also acts to decrease the convexity of the rail. The base must then be placed in tension also and consequently the web must be placed in compression. The locations of the neutral axes are indeterminate. They will depend, among other factors, upon the design of section and the relative rates of cooling of the head, web and base.

The head and base of the rail are therefore left in a state of internal tension and some central portion (the web) in compression. The exact distribution is not determinable.

Temperature Gradient between Surface and Center of Head

In the preceding discussion no mention has been made of the temperature gradient that exists between the outside surface and central portion of the head. During cooling the center is always at a higher temperature, the difference depending upon the rate of cooling.

For convenience, consider the head separately from the web and base. As cooling occurs the outside surface cools more rapidly than the inside. A temperature gradient is established. The outside will contract, thereby tending to induce a compressive stress on the central portion of the head and resultant tensile stress on the outer fibers. Due to the low strength and high plasticity of steel at temperatures above the transformation range, these stresses will be very small. When the outside layers reach the A_3 transformation, expansion occurs, which will relieve any tensile stress that may be present. The compression in the underlying metal, therefore, is relieved and possibly the metal placed into tension. As the underlying portions reach the transformation temperature, they in turn expand, relieving any stress on them, and in turn tend to pass a tensile stress on to the more central layers.

Just as the center emerges from the transformation range, it is evident from Fig. 30 that its rate of cooling is faster than the rate of cooling of the surface. The rate of contraction of a central portion of the head is then greater than in the surface layers. A tensile stress is therefore developed in the central portion of the head, which will be additive to any other tensile stresses that may be present at the same time. These stresses would be additive to those developed by the more rapid cooling of the base relative to the head.

It is evident from the above discussion that the stress distribution in a rail varies during the cooling in a complex and indeterminate manner. The magnitude of the stresses cannot be estimated without data regarding the temperature distribution during cooling, the modulus of elasticity of the steel during cooling, its yield point and other properties. Transverse stresses would also be present, as suggested previously by Howard.

Certain facts appear significant, however. It has been shown that, as the head of a rail cools through the temperature range just below the Ar transformations, tensile stresses in the head and base are caused by differential cooling. From Fig. 30 this range begins when the center is at about 670° C. A maximum temperature difference between edge of base and center of rail was noted for air-cooling when the center was at approximately 660° C. and the edge of base at 470° C. The base, at the latter temperature and below, will have a relatively high resistance to plastic deformation, especially as cooling enters the blue-heat range. On the other hand, the center of the head, at 660° C., is entering the secondary brittle range. The tensile strength, elongation and reduction of area of some rail steels are relatively low (Fig. 3) in this temperature range. The steel, therefore, is in an unfavorable condition to resist the tensile stresses imposed, and rupture may conceivably occur. The somewhat higher temperature of the center and consequently somewhat lower strength and ductility during the period that stress is developed may account for failure occurring internally, giving rise to transverse shatter cracks. The added internal tensile stress incident to the temperature gradient between center and surface of the head is also probably a contributing cause for internal failure.

Degree of Secondary Brittleness

The marked difference in the degree of secondary brittleness in different heats, its marked intensity in heat 3 (Fig. 3) from which a new rail was found to contain shatter cracks,[26] its equally marked intensity in rail from heat PO (Fig. 11)which failed by transverse fissure and showed shatter cracks and its presence in rail from heat CN1 (Fig. 12), which also showed shatter cracks, all tend to confirm the hypothesis that shatter cracks may be associated with secondary brittleness.

That a rail may have secondary brittleness and not show shatter cracks is indicated by rail from heat CN2 (Fig. 12). This rail was subjected to identical service with rail from heat CN1, which failed by transverse fissure and contained shatter cracks. The two rails were from different heats and so were rolled and cooled at different times. Both steels had secondary brittleness and therefore probably had a propensity to form shatter cracks. The degree of secondary brittleness, however, was not pronounced. The assumption seems reasonable that the rail (heat CN1) that developed shatter cracks may have been cooled at a relatively faster rate than the one from heat CN2, with the development of sufficiently higher stresses to cause rupture in the secondary brittle range. This indicates a rather critical "border line" condition in cooling rates when secondary brittleness is present. Obviously, if all

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[26] J. R. Freeman, Jr. and H. N. Solakian: *Op. cit.*, Fig. 26.

rails were cooled slowly enough to prevent the formation of internal stresses, shatter cracks, which admittedly constitute the relief of internal strains, would not be formed. It also seems evident that a rail steel having slight secondary brittleness, such as heat 21 (Fig. 7) should be less liable to failure under conditions of relatively rapid cooling than a steel having marked secondary brittleness. The tensile strength of this steel (heat 21) is approximately the same in its secondary brittle range as some of the other rail steels but because of its greater ductility in this temperature range considerable flow could occur and so relieve without rupturing any stress that might develop during cooling.

It is fully appreciated that the tensile properties of the steel of a rail at a given temperature during cooling may be different after rolling from the properties of the same material allowed to cool and then reheated to the given temperature and tested. For temperatures above the transformation range the refinement of grain and other changes incident to the Ac_{123} transformations would probably give different properties. That such a difference may exist at lower temperatures is indicated by the tests of specimens from heats 3 and PO, which were annealed at a temperature (700° C.) just below the Ac_1 transformation; this annealing caused a marked decrease in the degree of secondary brittleness. This fact indicates that secondary brittleness may be more pronounced during cooling than after cooling and reheating to the secondary brittle range.

In the tests of specimens from medium manganese rails (Fig. 15) it is evident that this steel shows marked secondary brittleness. It is known that steel of this type[27] has given excellent service in track and is reported to be almost free from shatter cracks and failures of the transverse fissure type. This appears to contradict somewhat the hypothesis that shatter cracks (nuclei for transverse fissures) may be associated with secondary brittleness, especially as rails from these heats have been reported[28] as giving good service in track. However, shatter cracks have been reported in intermediate manganese rail as the cause of horizontal crushed head failures, and transverse fissures have also been reported in rail steel of this type.[29] It would be of interest to determine whether such rail showed secondary brittleness. It is also true that shatter cracks are not necessarily present in a rail showing secondary brittleness; their formation depends on the rate of cooling of the rail.

The fact that secondary brittleness is found in other steels than rail steels suggests that other types of unexplained failure such as internal cracks in ingots or forgings, may be due to secondary brittleness.

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[27] Report of Rail Committee. *Bull.* Amer. Ry. Eng. Assn. (1929).

[28] Private communication from G. J. Ray, September, 1929.

[29] Report of Rail Committee. *Bull.* Amer. Ry. Eng. Assn. (1929). See data furnished by New York Central Railroad.

Hultgren[30] has shown for a ball and roller-bearing steel (0.70 C, 1.0 Cr, 1.0 Mn) that internal cracks when present invariably formed during cooling after the final hot-working operation and that their formation is prevented by retarded cooling. He suggested that shatter zones in rails were of similar origin. It is suggested that the cause of the development of internal cracks in the steel studied by Hultgren might have been due to secondary brittleness in the steel.

The data indicate that equalization of temperature and slow cooling of rails or other steel objects are desirable procedures to prevent formation of internal failure.

PRELIMINARY STUDIES OF CAUSE OF SECONDARY BRITTLENESS

It has been shown that secondary brittleness may be present in a relatively pure iron, rail steels, high-carbon steels and alloy steels. The low ductility has been shown to be related apparently to a grain boundary condition of the steel, as was indicated by the marked intercrystalline shattering found in specimens tested in the secondary brittle range. The cause, then, must be related to one or more of the following: some structural condition, an element, or nonmetallic inclusions that may be present in steels of widely varying composition. The influence of free cementite has been suggested. The fact that annealing below the Ac_1 transformation affects the degree of secondary brittleness indicates that it may be related to a constituent capable of solid solubility or precipitation at temperatures below the A_1 transformation.

Nitrogen analyses[31] have shown no relation of nitrogen content to degree of secondary brittleness. A few residue analyses[31] have been made and show no relation of degree of secondary brittleness to total Al_2O_3 or SiO_2 content. Secondary brittleness has been found in rail steels killed with aluminum and also in rail steels in which aluminum was not used. On account of difficulties in analytical methods for the determination of MnO or manganous silicate inclusions, an indicated relation to MnO content cannot yet be considered significant. Space is not available to report in detail on this phase of the problem at the present time. Detailed studies along the lines suggested are being carried out.

SUMMARY AND CONCLUSIONS

A study has been made of the tensile properties of rail steels and some other steels at elevated temperatures. Special study was made of the tensile properties in the approximate temperature range of 400° to 700° C. It

[30] A. Hultgren: Flakes or Hair Cracks in Chromium Steels with a Discussion of Shattered Zones and Transverse Fissures in Rails. *Jnl.* Iron and Steel Inst. (1925) **111**, 113.

[31] By J. S. Acken, U. S. Bureau of Standards.

has been found that the ductility of all rail steels, as measured by percentage elongation and reduction of area, decreases with increase in temperature over a portion of this temperature range. In some instances the decrease in ductility is marked, the elongation and reduction of area values becoming less between approximately 500° and 650° C. than at normal atmospheric temperatures. The same phenomena have been found to exist in Armco iron, a 1 per cent. carbon steel and some alloy steels. This range of temperature, in which low ductility becomes manifest, has been termed the "secondary brittle" range to distinguish it from the well-known "blue brittle" range occurring at 200° to 300° C. and the "hot-short" range which is usually associated with the A_3 transformation and high sulfur content. The phenomenon has been termed "secondary brittleness."

The degree of secondary brittleness varies markedly between individual heats and the temperature of the maximum effect also varies.

The data indicate that the secondary brittleness is not confined to individual rails or ingots but apparently is a property of the heat as a whole. It has been shown that the degree of secondary brittleness is decreased by annealing at a temperature (700° C.) slightly below the Ac_1 transformation as well as at the usual annealing temperatures above the Ac_3 transformation.

The cause of secondary brittleness has not been determined. Residue analyses and analyses for nitrogen content indicate that the phenomenon is not related to silica, alumina or nitrogen contents. Some evidence has been obtained which indicates that it may be related to the MnO content or free carbides.

Data are also given in the report on the rate of cooling and temperature distribution in a 130-lb. P. S. section rail during cooling in still air, moving air, and during quenching in cold and hot water.

A hypothesis as to the formation of shatter cracks in rails, based on the phenomenon of secondary brittleness and temperature distribution during cooling, is presented. Rapid cooling through the secondary brittle range is believed to cause the formation of shatter cracks in rails showing secondary brittleness. Shatter cracks are believed by many to be the nuclei of transverse fissures. It is, therefore, suggested that the origin of transverse fissures is related to secondary brittleness and rate of cooling of the rail.

The fact that secondary brittleness is found in other steels than rail steels suggests that other types of unexplained failures, such as internal cracks in ingots or forgings, may be due to secondary brittleness.

The data indicate that equalization of temperature and slow cooling of rails and other steel shapes through their secondary brittle range are desirable procedures to follow in order to prevent formation of shatter cracks.

DISCUSSION

H. W. GILLETT, Columbus, Ohio (written discussion).—To those of us who believe that shatter cracks in rails are likely to act as nuclei for transverse fissures, this paper appears important, perhaps even epoch-making.

If testing for secondary brittleness at high temperatures will pick out heats of steel, which are indistinguishable by analysis, structure or mechanical tests at room temperatures, but which really differ in propensity toward shatter cracks, and if shatter cracks are a major cause of transverse fissures (which is at least a logical assumption), a powerful weapon is put into the metallurgist's hands. He can search for an underlying cause of transverse fissures without waiting for track service results. Best of all, the method would search out the *propensity* toward shatter cracks while the other new tool, the Sperry detector, has to have at least the crack, and preferably the fissure, actually present. Since the propensity may be there but may not actually have caused shatter cracks because of slow cooling, conclusions as to the effect of steelmaking variables, or whatever the underlying causes may be, might readily be obscured in the correlation of service data. Indeed, some such obscuring factor must be present, else the vast amount of service data that have been collected would, ere this, have led to the cause.

Since it is obvious that extensive use should be made of this method of study, it seems pertinent to suggest that some attention might be paid to a possible shortening of the test method of evaluating a steel as to secondary brittleness. The tensile strength curves are quite smooth through the range 300° to 650° C.; the variations appear in the ductility curves. If we can adopt the usual conception that an impact test gives figures that are a function of strength and ductility, then impact values over the secondary brittle range should also reveal the brittleness, though probably not as markedly as do the ductility curves.

It would appear, from the point of view of high-temperature testing, both quicker and simpler to make an impact test at these temperatures than to make a tensile test. It would be extremely interesting if the Bureau would make high-temperature impact tests on some of these steels and compare the curves with the ductility curves of the present paper.

The scatter of duplicate impact tests might make the data less reliable, and it was correct to go through the series, in these pioneer studies, by tensile testing alone. That having been done, the subject appears important enough to justify looking next for a correlation between the ductility and the impact curves.

G. W. QUICK.—In regard to the question of impact tests at elevated temperatures, we have done nothing along that line as yet. The point is well taken and we have it in mind. It has come to our attention recently from other sources besides from Dr. Gillett, and it remains for subsequent tests to give information on that point, and I presume that we will try some impact tests in the near future to ascertain whether they would be of much value as a quick test for secondary brittleness in steels.

R. O. GRIFFIS, Ashland, Ky.—I should like to say that some excellent work in regard to the aging and blue brittleness of iron and steel was published in *Stahl und Eisen* in 1919 by Dr. Fettweiss. He brought out the important fact that the primary blue brittleness is not obtained by an impact test. It is obtained only by a test slow enough to allow the transformation that brings about blue brittleness to take place while the test is being made. In my opinion, therefore, impact tests in this connection would not show what the tensile tests do.

A. SAUVEUR, Cambridge, Mass.—This paper is likely to be fruitful in important results. I regret that I did not have the opportunity of seeing the paper before attending the meeting, as I believe I could have brought with me some of the results of our own work in investigating the properties of steel at elevated temperatures at Harvard, which would have shown that in many of the steels used in our investiga-

tions decreased ductility in the vicinity of 600° C. had been observed.   These results were described in my Campbell lecture[32] last September.

Referring to the authors' statement (p. 233) that the tensile properties of steels in the temperature range of 500° to 700° C. had not been studied intensively, it is proper to remark that the strength and ductility of steel within that range of temperature has been studied extensively by us, using the torsion test, which, of course, is as satisfactory as a tensile test to bring out discontinuation in strength and ductility.

From the authors' results and from our own, I am inclined to believe that most steels exhibit decreased ductility in the vicinity of 600° C., although in different degrees.   It is in no way peculiar to rail steel.   Indeed, it would appear as though the steel free from this characteristic, called by the authors "secondary brittleness," is rather abnormal.

Let us recall that nickel-chromium steel, of the so-called 18-8 type, that is, containing 18 per cent. of chromium and 8 per cent. of nickel, also exhibits reduced ductility in the vicinity of 600° C., as reported by Dr. Lester Strauss and others.

The authors tested but one steel in the cast condition and report the occurrence of secondary brittleness "to a relatively moderate degree."   Further testing of steel in the cast condition will be required before we are justified in expressing the belief that secondary brittleness is caused by work.

The authors' finding that annealing even below the A point results in the increased loss of ductility in the secondary brittleness range should be of considerable significance.   I should like to offer a possible explanation of the occurrence of this temporary loss of ductility within a narrow range of temperature.

I have in mind the recrystallization of work-hardened steel as the possible cause. To make the matter clear, subjecting steel to tensile stress above its elastic limit at a temperature of 500° C. produces a certain amount of cold work, and recrystallization should take place if the temperature were high enough.   In view of the relatively small amount of cold work produced, however, a temperature of 500° C. is too low, and recrystallization does not take place.   Stressing at 600° C., however, is sufficient to cause recrystallization and we may assume that this phenomenon while taking place temporarily reduces the ductility of the steel.   Stressing at 700° C. or at higher temperatures does not cause any work hardening and therefore would not be accompanied by recrystallization and temporary loss of ductility.

In short, the phenomenon would be due to the coexistence of a critical strain and of the critical temperature required to cause recrystallization.   This explanation is offered tentatively, with full realization that it is highly speculative.

The authors' able discussion of the possibility of shatter cracks in rails and transverse fissures being due to the existence of secondary brittleness is of much importance.   If they are right, a distinct advance will have been made in the solution of this troublesome problem.

The statement that the fracture in the brittle range is intercrystalline should not be a cause for surprise.   It indicates that we have now passed the recrystallizing temperature, and I think it is well known that above the recrystallizing temperature fractures are generally intercrystalline, on the ground that then the crystalline phase is now stronger than the amorphous phase.

A. V. DE FOREST, Bridgeport, Conn.—In regard to the possible explanation of shatter cracks being due to a decrease in ductility, it seems to me that it is necessary to show that this decrease is down nearly to the elastic deformation.   Otherwise a very small plastic strain will readjust the stress below the danger point.   It may be

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[32] A. Sauveur: Strength of Steels at High Temperatures.   Campbell Memorial Lecture.   *Trans.* Amer. Soc. Steel Tr. (1929) **16**.

possible that the elongation decreases much below the 5 per cent. figure, if smaller areas are considered. In this case the brittle-range explanation is preferable.

If, on the other hand, the elongation of a specimen of very small diameter still remains in the region of 5 per cent., other evidence must be brought up. Perhaps a series of specimens of decreasing diameter would show whether there is a tendency in this direction. I would like to know whether this is possible or whether it has been tried.

R. JOB, Montreal, Que.—In presenting the paper, Mr. Freeman spoke particularly about the development of transverse fissures and of the likelihood that the characteristic brittleness of the steel extended through the entire heat. It has been my own experience, and, I think, general experience, in connection with the formation of fissures that they do not ordinarily develop throughout the entire heat but only in individual rails. In other words, there are usually comparatively few failures of this type in a heat, and the remainder of the heat is generally free from fissures. This condition can be determined easily by placing rails head down in the drop-testing machine. Even a relatively light blow will cause the steel to snap if a fissure is present, and when there are several fissures, the rail is likely to fly apart in a number of pieces as a result of the vibrations set up by the single blow.

The results of Mr. Freeman's research indicate the great advantage to be derived from some simple test at the mills to determine whether or not "secondary brittleness" to an objectionable degree is present in the steel. Work with this object in view might be carried on profitably at the U. S. Bureau of Standards and elsewhere.

Transverse fissures, as we all know, were found more than 30 years ago in low-carbon steel of about 0.25 per cent. carbon, and we have had them with us ever since. The practical value of the present paper lies in the fact that it goes a step beyond previous investigations and brings into view one of the underlying principles of weakness inherent in fissured steel. Conversely, it affords a possible means of determining whether or not fissures are apt to develop in a given lot of rails. Having this knowledge, it should be possible without great difficulty to locate in the mill the place and the conditions under which "secondary brittleness" develops so that suitable corrective measures may be devised and put into effect in the manufacture of rails. This would undoubtedly be a distinct step forward in the manufacture of better steel.

A. L. DAVIS, Waterbury, Conn.—There may be a possible way of detecting the tendency to fissure cracks. Instances have been observed in 0.28 per cent. carbon Bessemer steel (in which segregation existed due to the position in the ingot) where a hot-rolled bar on subsequent cold drawing developed transverse internal fissure cracks every two or three inches. Cold drawing might give a means of detecting the tendency to fissure cracks in a heat of rail steel. By cutting out a specimen from the head of a rail and giving it a severe cold draw, any incipient fissure cracks would undoubtedly make themselves apparent.

I agree with Mr. Freeman that the normal elongation does not apply in protecting against fissure cracks. A different action takes place when the center of the piece is asked to do something different from the outside; that is the case in cold drawing, where there is transverse compression plus tension at the surface and pure tension near the center of the bar.

YAP, CHU-PHAY, New York, N. Y. (written discussion).—This paper is an important contribution to our knowledge of steels at high temperatures, particularly because it gives the complete history of the steels used in the experiments. I believe the authors have given conclusive evidence that there is a secondary brittleness range at 500° to 650°C. As far back as 1924, I noticed this peculiarity in one of Dr. Honda's

papers,[33] and was curious as to what might have caused it. Later, various papers by Dr. Honda and his associates at the Tohoku Imperial University (on decomposition of martensite, tensile strength at high temperatures, etc.) showed occasionally the minimum point in elongation and reduction in area at about the same temperature. If I interpret their conclusions correctly, they attribute it to recrystallization of ferrite.

I have shown previously [34] the phenomenon of age-hardening in mild steel (0.10 per cent. carbon). The curves are herewith reproduced (Fig. 39). The maximum hardness was obtained in the 600° C. anneal after about 18 hr. This is particularly striking if we take into consideration that actually the grain size has increased more rapidly than that in the 700° and 800° C. anneal. This phenomenon I naturally connected with the limited solubility of carbon in ferrite (Fig. 40).

In this study I also subjected some pieces from the same melt (not rolled into strips) to compression at 10,000, 20,000 and 30,000 lb. load and then annealed them at various
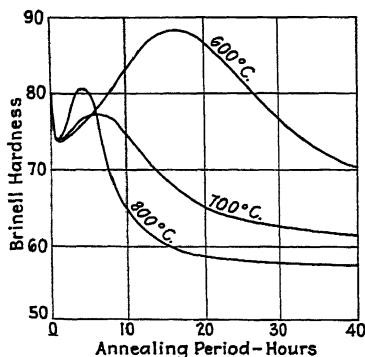
FIG. 39.—ANNEALING PERIOD VERSUS HARDNESS; NOTE AGE-HARDENING.
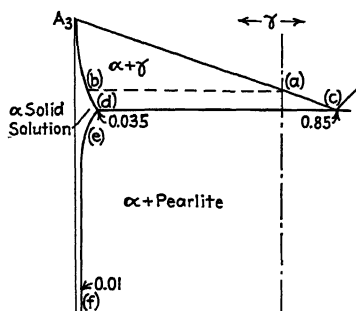
FIG. 40.—SOLID SOLUBILITY OF CARBON IN FERRITE (α).

temperatures in 100° C. intervals. Other duties prevented me from following up this particular phase of the work, but it is interesting to note (Fig. 41) that the blue-heat range as well as the secondary brittleness range are indicated. If the second maximum is due to recrystallization and refinement of the grains, why is it nearly constant, instead of being displaced towards a lower temperature? We know that recrystallization temperature decreases directly in proportion with the amount of strain and cold work.

I shall make some bold suggestions in regard to a possible explanation of the secondary brittleness described by Freeman and Quick. From Fig. 40 we notice that as the steel (say, one containing 0.70 per cent. C) cools to (a), pre-eutectoid ferrite will form, containing (b) amount of dissolved carbon, and just before A_1 takes place, the ferrite would contain (d) amount of carbon—about 0.035 per cent. When pearlite is formed, it is composed of cementite and ferrite, but the ferrite contains about 0.035 per cent. carbon. Upon further cooling, the dissolved carbon in the pre-eutectoid ferrite is precipitated perhaps as boundary carbide (a term due to Pilling), or, as is more likely, colloidal carbide. Normally at room temperature ferrite contains less than 0.01 per cent. carbon. My X-ray studies on lead solders have convinced me that the lead in the eutectic contains about 5 per cent. Sn, because its lattice parameter is that of a 95 Pb-5 Sn alloy.

[33] K. Honda: Forging Temperature of Steels. *Sci. Repts.* Tohoku Imp. Univ. (1924) **13**, 21.

[34] Yap, Chu-Phay: On Grain Growth in Mild Steels. *Trans.* Amer. Soc. Steel Tr. (1927) **12, 609.**

The question may be legitimately raised as to what becomes of the carbon in the eutectoid ferrite upon cooling. The pearlite grain is a stable structural constituent, consequently the carbon in the ferrite cannot be precipitated but must remain in enforced solution. The formation of pearlite takes place theoretically at a constant temperature. We must also not overlook the fact that the pre-eutectoid ferrite acts as a network around the pearlite grains. A real equilibrium requires the complete segregation into structural units of the pre-eutectoid ferrite and the pearlite grains, but this is seldom obtained in steels above 50 per cent. pearlite by volume (0.40 per cent. C). We also notice many a time that in lower carbon steels the pearlite is often of the kind known as sorbitic pearlite, unless the steel has been cooled slowly, in which case we obtain the normal lamellar pearlite. If the cooling has been too slow, we obtain divorced pearlite (the first stage of spheroidization). Perhaps the reason we often obtain sorbitic pearlite when the cooling through A_1 is fairly rapid is that the pearlite grain is not sufficiently strong structurally to prevent the precipitation of carbon from the eutectoid ferrite.
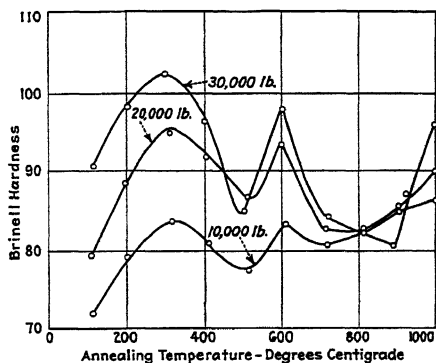
FIG. 41.—HARDNESS VERSUS ANNEALING TEMPERATURES OF MILD STEEL SUBJECTED TO COMPRESSION.
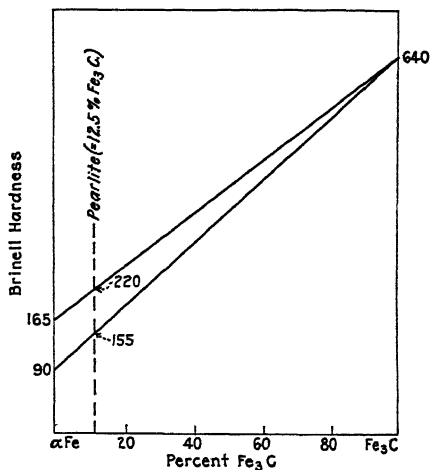
FIG. 42.—HARDNESS OF PEARLITE AND ALPHA IRON BY RULE OF MIXTURE.

If pearlite were merely a mechanical mixture of ferrite and cementite, the law of mixture would hold in regard to its hardness. In Fig. 42, the hardness of pearlite, which contains 12.5 per cent. cementite, is 155, if we use Tamaru's hardness for ferrite as 90 (which seems a little high) and cementite as 640 [Sci. Repts., Tohoku Imp. Univ. (1926) 15, 829]. The hardness of pearlite is around 220, to obtain which the value of ferrite must be 165. The rule of solid solubility (Norbury) is that the more limited the solubility, the greater the hardening power per unit solute. By the way, the hardness of austenite is about 155, which is lower than ferrite with dissolved carbon.

Suppose that in cooling rapidly through the A_1 zone (as in air cool), two conditions exist; namely, (1) the pre-eutectoid ferrite may carry in solution 0.035 per cent. carbon without precipitation, and (2) the pearlite grains will be finer and therefore the ferrite in the intercrystalline boundary will be thinner. The precipitation of cementite involves a slight contraction, and since the pre-eutectoid ferrite is in the grain boundary, one may draw his own conclusion regarding its structural weakness when the carbon is reprecipitated upon subsequent heat treatment under the effect

of a tensional strain. A normal reanneal followed by slow furnace cooling allows equilibrium to be established.

A study of the data offered by Messrs. Freeman and Quick shows the following general relationship:

1. When the plain carbon steel is around 0.60 per cent. C, the brittleness is located at about 500° to 550° C., while those of the eutectoid composition and those with other alloying elements show the brittleness to be at 600° or above.

2. When the steel is cooled slowly from the forging temperature (ST-2) the range is shifted to about 680° C.

3. One poured from a very high temperature (S-17) shows the brittleness temperature to be at 650° C. Its history is not given.

In other words, the zone of secondary brittleness is quite variable. According to my theory of precipitation of the cementite by the ferrite, those steels with 0.50 to 0.60 per cent. C should show fracture along the intercrystalline ferrite, which becomes structurally weak at around 500° to 550° C. when it precipitates its dissolved carbon. The eutectoid steel requires a higher temperature before the effect of tension can bring about the precipitation of the dissolved carbon from the eutectoid ferrite and the consequent disruption of the pearlite grains. We all know that it is easier to spheroidize the cementite in pearlite by first subjecting the steel to mechanical cold working. Fig. 26 certainly gives evidence of intracrystalline rather than intercrystalline fracture. Yamada[35] has shown that between 0° to −200° C., the fracture in ferrite and pearlite is intracrystalline and that the least brittle steel is one in sorbitic condition.
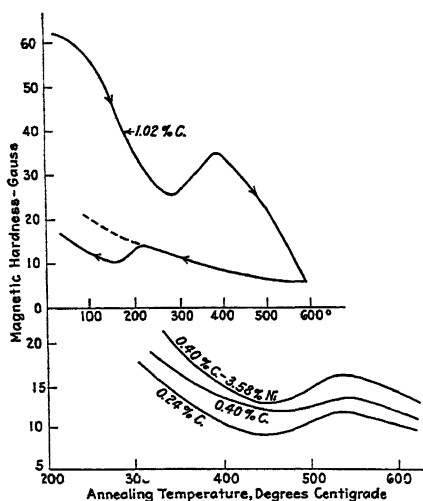

FIG. 43.—MAGNETIC HARDNESS VERSUS ANNEALING TEMPERATURE. (MATSUSHITA AND NAGASAWA.)

The line, A$_s$-d-e-f, showing the limited solubility of carbon in ferrite, seems so insignificant, yet as I stated in my paper in 1927, it may some day explain temper brittleness. I suggest that a study of low-nickel alloys be made, because the equilibrium diagram of Fe-C-Ni has already been worked out completely by Kasé.[36] The limited solid solubility range gradually narrows with increasing nickel content until it disappears at about 10 per cent. Ni. I am inclined to believe that chromium and manganese have the same effect, but phosphorus, oxygen, and possibly copper widen the range.

Honda and his school have done wonderful work by means of magnetic analysis. They have evolved a method of magnetic hardness testing, which they applied to the study of the decomposition of martensite upon tempering. They claim that when the precipitated carbon begins to build its own crystal lattice, there will be an increase in the magnetic hardness of the steel as shown in Fig. 43. The magnetic

[35] R. Yamada: On the Impact Test of Steels at Low Temperatures. *Sci. Repts.*, Tohoku Imp. Univ. [1] (1926) 15, 631.

[36] T. Kasé: On the Equilibrium Diagram of the Iron-Carbon-Nickel System. *Sci. Repts.*, Tohoku Imp. Univ. [1] (1925) 14, 173.

hardness curves of three steels given by Matshushita and Nagasawa[37] show a maximum point at about 530° C. However, they attribute it to recrystallization. According to Satô,[38] there is a slight heat evolution noticeable at that point, 530° C. or thereabout. I believe this heat evolution is due to the precipitation of cementite from the ferrite. I have calculated the heat evolution to be of the order of 5° per gram.

R. Job (written discussion).—In connection with the recent work at the U. S. Bureau of Standards by Freeman and Quick, on transverse fissures in rails, I should like to suggest the investigation of another type of defect, which may be termed "longitudinal fissures." In these failures a strip of metal about ½ in. deep, often extending from side to side of the rail, splits off from the top of the head. The pieces are sometimes several feet long and at times occur at intervals along an entire rail. A break in the steel, appearing like a seam, extends along the bottom of the fracture,
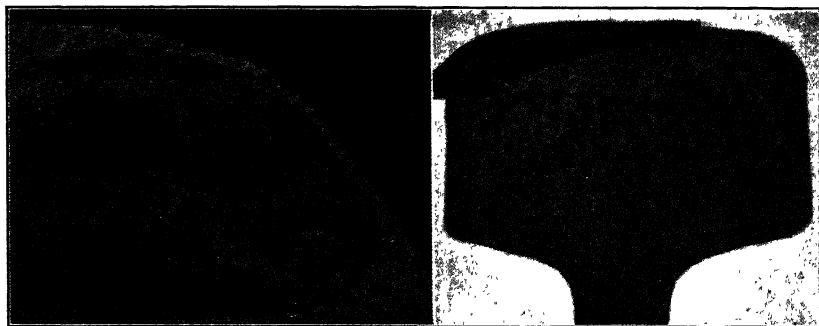
FIG. 44.—THE HEAD OF THE DEFECTIVE FIG. 45.—FAILURE SIMILAR TO THAT
RAIL.   IN FIG. 44.

near the middle of the head and about ½ in. below the surface, and progressive failure is indicated clearly by the characteristic growth-rings.

This type of failure is an old one, well known to railroad engineers. The general condition is shown in several illustrations in a paper[39] presented to the International Congress for Testing Materials at New York in 1912. Fig. 44 shows the appearance looking down upon the head of the rail. Fig. 45 shows another failure of this type and Fig. 46 still another. Fig. 47 is from the same rail as Fig. 44. The section was polished and lightly etched with iodine. It indicates the unsound, seamy condition which we found characteristic when these failures occurred. Tensile tests taken across the head transverse to the direction of rolling would indicate clearly the unsoundness of the metal.

My suggestion would be that the Bureau of Standards first investigate the condition of failed rails of this type and then trace back the defects to the precise point at which they are formed in the manufacture of the steel, and finally indicate clearly the means that should be adopted to ensure the elimination of the defects from the finished rails.

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[37] T. Matshushita and K. Nagasawa: On the Phenomenon of Temper-Hardening in Steels. *Sci. Repts.*, Tohoku Imp. Univ. [1] (1927) 16, 639; On the Mechanism of Tempering of Steels. *Ibid.*, 901.

[38] S. Satô: On The Thermal Analysis of Quenched Carbon Steels. *Sci. Repts.*, Tohoku Imp. Univ. [1] (1929) 18, 303.

[39] R. Job: Some Defective Rails and How to Avoid Them. *Iron Tr. Rev.* (1912) 51, 504–505.

Within comparatively recent years many well-recognized improvements have been devised in the manufacture of steel, rendering possible the production of a product which is much more clean and solid and free from nonmetallic inclusions and segregation, but in the case of rails, which are of vital importance to the traveling public, there appears to have been an evident tendency to follow along the lines of least resistance—and of greatest tonnage—without effective action toward eliminating defects that are known to exist.

I feel sure that the railroads would cooperate heartily with the Bureau in a constructive investigation of this type, and there would be no difficulty in securing rails showing the characteristic forms of failure.

J. R. FREEMAN, JR. (written discussion).—The discussion and kind remarks regarding the work presented by Dr. Gillett are greatly appreciated. Much of the work was carried out during his administration as Chief of the Division of Metallurgy and we are indebted to Dr. Gillett for the benefit of many helpful discussions and his enthusiastic support in carrying it forward.
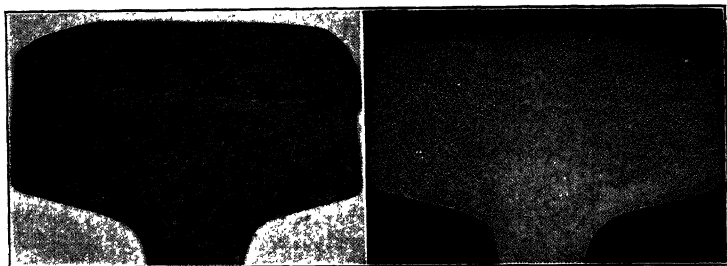
FIG. 46.   FIG. 47.

FIG. 46.—FAILURE SIMILAR TO THAT IN FIG. 44.

FIG. 47.—ANOTHER SECTION OF RAIL SHOWN IN FIG. 44. POLISHED AND LIGHTLY ETCHED WITH IODINE.

Mr. Griffis' remarks regarding the effect of the rate of testing in the impact test on blue brittleness are pertinent and may hold true in the "secondary brittle" range.

It is pleasing to note the confirmation of our results obtained by Dr. Sauveur under the rather markedly different conditions of a torsion test. The present paper was written previous to the time of his Campbell Memorial lecture and copies of this talk unfortunately were not available before the presentation of the paper, so that comparisons could not be drawn. Dr. Sauveur's theory of the cause of "secondary brittleness," admittedly speculative, is suggestive and should be investigated further. The fact that fracture in the secondary brittle range is markedly intercrystalline tends to support the theory, for at that critical temperature for a given critical condition of stress at which recrystallization is occurring it is reasonable to believe that grain-boundary conditions are in an unstable state that may readily permit intercrystalline failure to occur.

Dr. de Forest is right in the assumption that elongations of as little as 5 per cent. in the secondary brittle range should be sufficient to relieve any thermal stress that might develop during cooling of the rail, but it must be borne in mind that the elongation values recorded were measured over the usual·length of 2 in. and are a summation of the properties over the entire test section. Locally the ductility may be much less. This is indicated by the low reduction of area in the secondary brittle range. Also, as pointed out in the paper, a point in the head of a rail during cooling is subjected to transverse as well as longitudinal stresses.

Mr. Davis' suggestion of determining the presence of shatter cracks by cold drawing might show their presence in the particular rail tested but the fact that a particular rail has or is free from shatter cracks is no indication of their prevalence in the remaining rails in the heat.

A discussion on rail steels by Mr. Job is always welcome. His observation that fissures do not ordinarily develop throughout a heat has been shown to be true many times. The fact that fissures do not develop in all rails of a heat does not indicate that all of the rails would not show secondary brittleness if tested at elevated temperatures. As brought out in the paper, the development of shatter cracks (nuclei for transverse fissures) is dependent first upon degree of secondary brittleness and then upon the rate of cooling of the rail through the secondary brittle range. It is believed that a heat of rails may show marked secondary brittleness and yet if cooled slowly through the secondary brittle range, so as to prevent the development of thermal stresses, shatter cracks (nuclei for transverse fissures) would not develop. However, if all of the rails in a heat showing secondary brittleness are not cooled under similar conditions it is conceivable that a few, perhaps only one or two, may cool sufficiently rapidly to develop sufficient thermal stress to cause internal rupture, shatter cracks, which later under the repeated stresses of service develop into transverse fissures. The remaining (relatively slowly cooled) rails of the heat, not having developed shatter cracks, would give normal service life.

Endurance Properties of Steel in Steam

By T. S. Fuller,* Schenectady, N. Y.

THE experiments described in this paper constitute the preliminary work of an investigation outlined to determine the combined effects of steam and temperature on the endurance properties of certain steels. Essentially of a fundamental nature, it was found necessary, in order to make the investigation comprehensive, to test materials treated to give a wide range of properties. The work reported deals chiefly with nickel steel with one series of tests including nitriding steel. Such a study involves numerous variables, and requires an endurance-testing machine of rather special design.

Testing Machines

The testing machines used were designed by C. E. Weaver;[1] they are a modification of the White-Souther and McAdam types. Each was driven directly by an individual ½-hp. 115-volt direct-current motor, running at a speed of 2200 r.p.m. Fig. 1 shows the assembly drawing and Fig. 2, a photograph of one of the machines. Specimen B is held by the rotating specimen holder A inside the steam box F, which is closed at the top by a tight-fitting, elliptical cover G. The load is applied to the specimen through the rod D and bearing C. E is an oil pipe leading from the lubrication system to the bearing C. The steam, which comes from the power house, is admitted through an inlet (not shown in Fig. 1) at the side of the box, the drain being at the bottom. Steam packings were placed around the rod D and the rotating shaft at H, from which the water was drained by means of a vacuum, which usually showed a gage reading of about 10 in. The temperature was measured by a mercury thermometer, and the pressure by a steam gage.

Method of Applying Load

After the motor has been started and the specimen as a consequence put in rotation, the load is applied by placing the foot pedal A (Fig. 2) in contact with electromagnet B, the winding of which is connected electrically in series with the motor. This operation releases the support under the weights that constitute the load. By this means the load

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LENGTH OF PIPE WHEN ASSEMBLING TO BE SUCH THAT WHEN NUT IS DRAWN DOWN, LOWER SURFACE OF WASHER WILL BE IN CONTACT WITH STEAM BOX FLANGE, BUT PERMIT A SLIDING FIT.
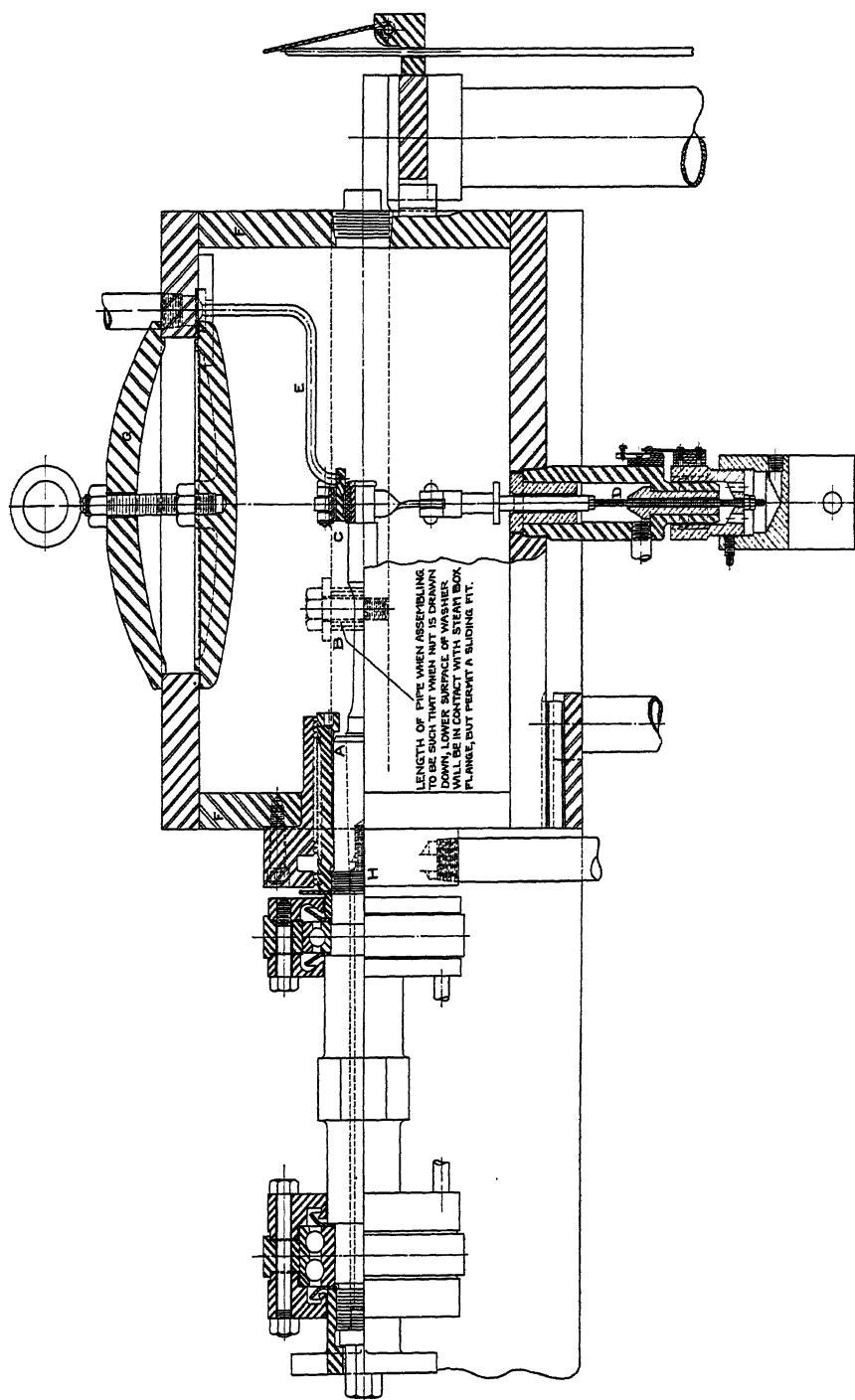
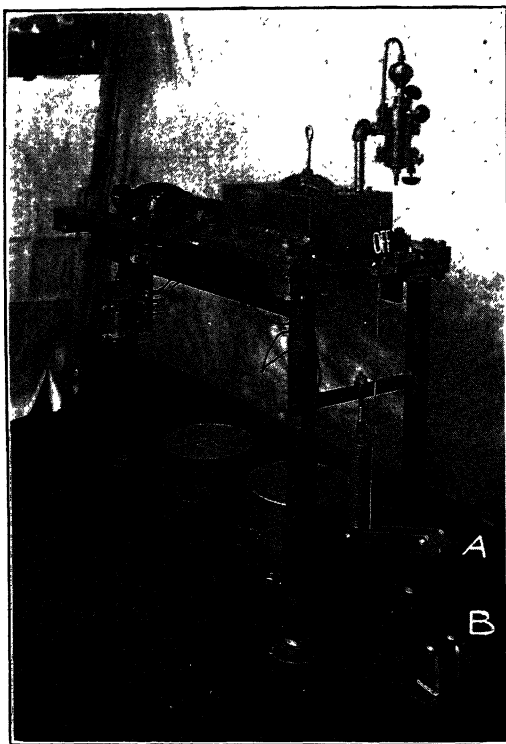FIG. 1.—ASSEMBLY DRAWING OF STEAM-FATIGUE TESTING MACHINE.

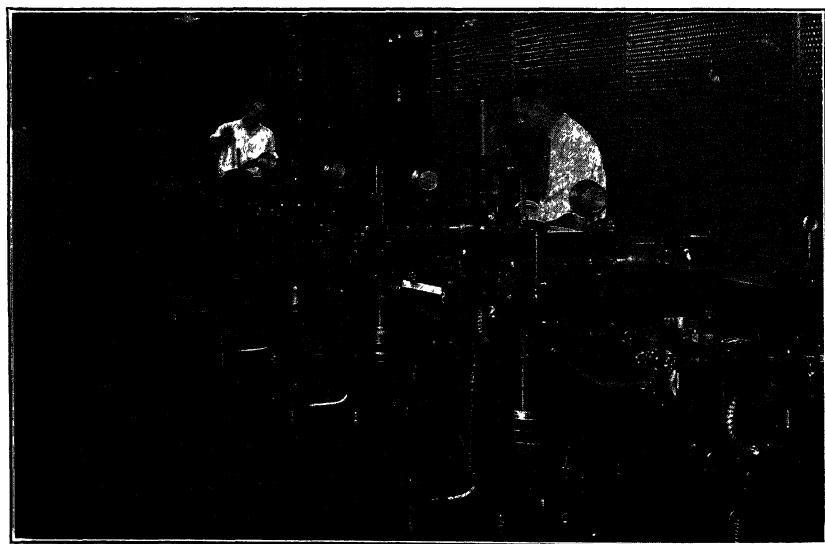FIG. 2.—STEAM-FATIGUE TESTING MACHINE.

FIG. 3.—SEVEN FATIGUE-TESTING MACHINES OF ROTATING-CANTILEVER TYPE.
Testing turbine bucket material in steam under actual conditions of pressure,
superheat or moisture.

remains on the specimen until manually released, or until the motor circuit is opened, whereupon the electromagnet immediately liberates the pedal and the load is removed from the specimen by a heavy spring. Should the power fail, this device insures the removal of the load before the specimen stops rotating.

Seven machines of the type described were used in this investigation; six were provided with steam boxes and one was without the box, so that it could be used for tests in the atmosphere. The arrrangement of the seven machines in the test room is shown in Fig. 3.

Specimens and Material

The type of specimen used is shown in Fig. 4. It is a rotating canti-lever beam, the reduced section of which is similar to McAdam's[2] type C specimen described in 1921. The maximum stress is in the plane whose
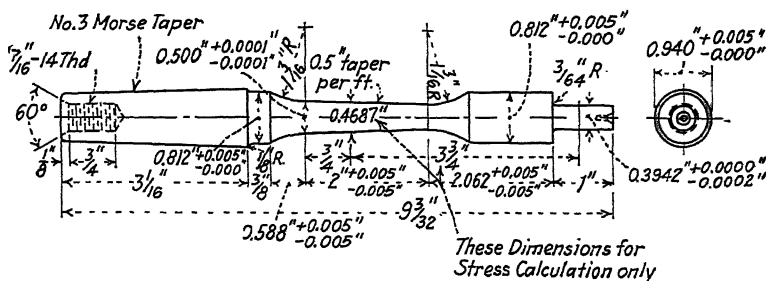
FIG. 4.—TYPE OF SPECIMEN TESTED.

diameter is 0.4687 in., although the stress from the bottom of the fillet over a distance $1\frac{1}{2}$ in. therefrom varies only $1\frac{1}{2}$ per cent. The end of the specimen that fits into the chuck is ground to conform to a standard No. 3 Morse taper.

The materials, which were 3.5 per cent. nickel steel containing 0.35 carbon and a nitriding steel, were received in the form of bars of 1 in. dia. and about 12 ft. long. Two tensile specimens were taken, one from one end and one from the center of each bar, the remainder being cut into $9\frac{3}{16}$-in. lengths for endurance specimens. All specimens were stamped with a letter indicating the material, with a number indicating the bar, and with another letter indicating the position of the specimen in the bar. After heat treatment, the specimens were carefully machined, special precautions being taken to remove the metal from the reduced section a little at a time in light cuts to avoid disturbing the structure underneath the surface. The final finishing on the reduced section was done with a Norton grinder, which was provided with two formed wheels to produce the exact contour of the specimen. The wheel performing the

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[2] D. J. McAdam, Jr.: Endurance of Steel under Repeated Stresses. *Chem. & Met. Eng.* (1921) **25**, 1081.

rough finishing operation was known as No. 60 K Crystollon, and the one employed for the final finish was 400-grain Grade 2 Crystollon shellac wheel, both being furnished by the Norton company. A lubricant, also made by the same company, known as "economy grinding lubricant" was used.

A comparison of results obtained with nickel steel specimens finished by this method of grinding with those of specimens of the same material prepared with 00 emery is shown in Fig. 5. The difference in values given by the two series of specimens is less than the experimental error.
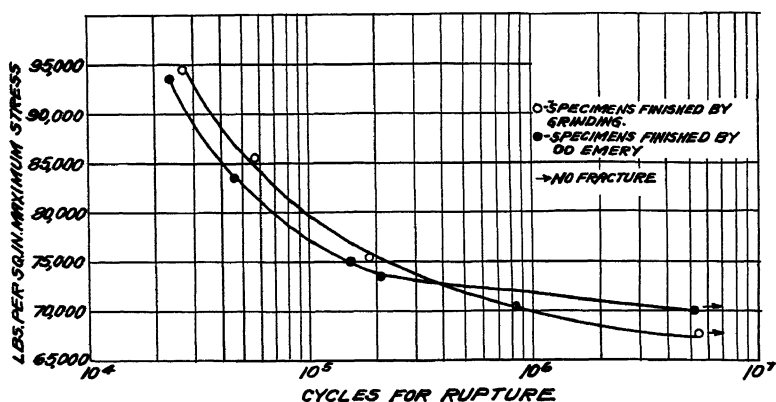
FIG. 5.—S-N DIAGRAM FOR NICKEL STEEL B, IN THE ATMOSPHERE AT ROOM TEMPERATURE.

HEAT TREATMENT AND PROPERTIES OF NICKEL STEEL

All specimens, including those for the tensile tests, were heat-treated before machining, all from one bar being treated together in the same furnace at the same time. Two series of tests were made, one on material treated to have low physical properties, hereinafter designated as nickel steel A, and another treated to have higher properties, hereinafter designated as nickel steel B. The properties are given in Table 1.

TABLE 1.—*Physical Properties of Nickel Steel Specimens*

Material	Ult. Str., Lb. per Sq. In.	Elas. Limit, Lb. per Sq. In.	Elong. in 2 In., Per Cent.	Reduc. of Area, Per Cent.	Brinell Hardness	Charpy Value (Keyhole Notch), Ft.-lb.
Nickel steel A	105,000–108,000	59,000– 67,000	24–27	57–61	218–238	21.5–22.2
Nickel steel B	115,200–125,000	92,000–102,500	24–26	65–69	255	34.6–36.1

METHOD OF TEST

The method followed was to load the first specimen of a series to be tested under any given set of conditions with a stress calculated to cause

failure in a comparatively short time. The load of successive specimens was then decreased in decrements of 5000 lb. per sq. in., until a stress was found at which the specimens withstood 50×10^6 cycles without fracture. This load value has been termed the endurance limit in these tests. Temperature and pressure readings were recorded at ½-hr. intervals.

MICROSTRUCTURE AND FRACTURE

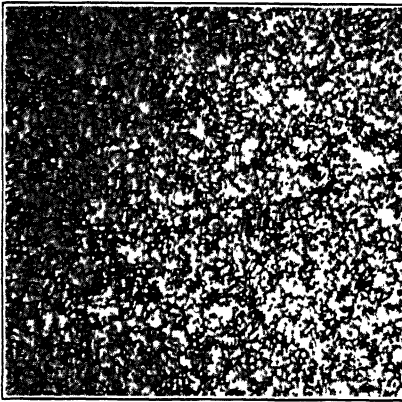Fig. 6 shows the microstructure of nickel steel B, and Fig. 7 a fracture typical of those obtained in these tests.

FIG. 6.—NICKEL STEEL B. × 200.   FIG. 7.—TYPICAL FATIGUE FRACTURE × 3.6.

TEST DATA AND RESULTS

A summary of the experiments is to be found in Table 2, and the data from which the endurance limits were determined have been plotted in Figs. 8–14.

The endurance limit of nickel steel A was found to be 45,000 lb. per sq. in. at room temperature in the atmosphere, and 35,000 lb. per sq. in. in 60 lb. steam at 150° to 160° C.

TABLE 2.—*Summary of Experiments*

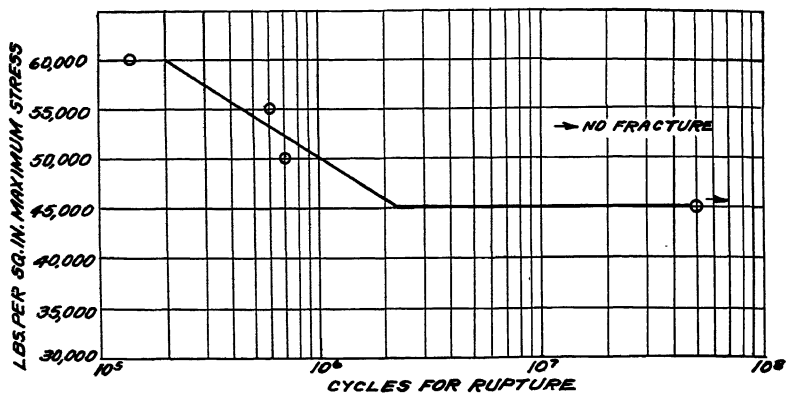| Material	Condition of Test	Endurance Limit, Lb. per Sq. In.
Nickel steel A..............	Air, room temperature	45,000
	Steam, 60 lb. 150°–160° C. (302°–320° F.)	35,000
Nickel steel B..............	Air, room temperature	55,000
	Steam, 98° C. (208° F.)	55,000
	Steam, 60 lb. 150°–160° C. (302°–320° F.)	50,000
	Steam jet in atmosphere	20,000
Nitrided steel..............	Steam, 60 lb. 150°–160° C. (302°–320° F.)	65,000

Fig. 8.—S-N diagram for nickel steel A, in the atmosphere at room temperature.
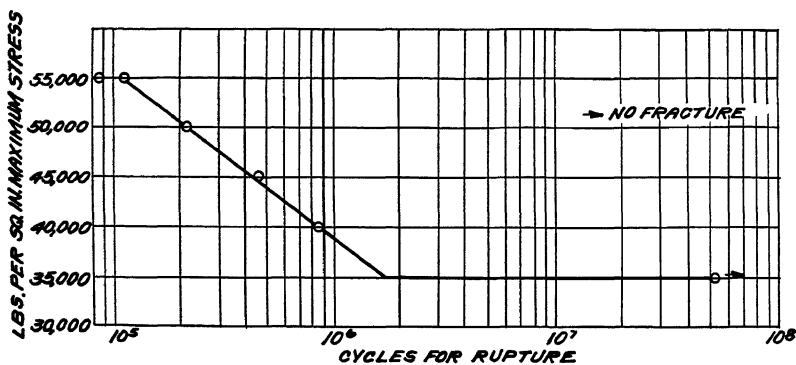

Fig. 9.—S-N diagram for nickel steel A in 60 lb. steam at 150° to 160° C. (302° to 320° F.).
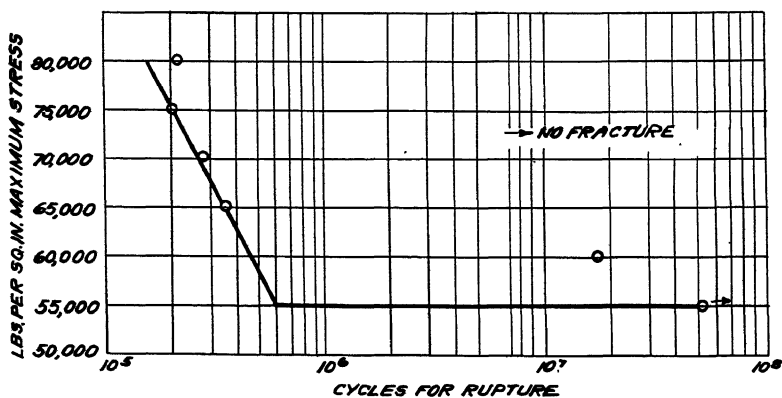

Fig. 10.—S-N diagram for nickel steel B in the atmosphere at room temperature.
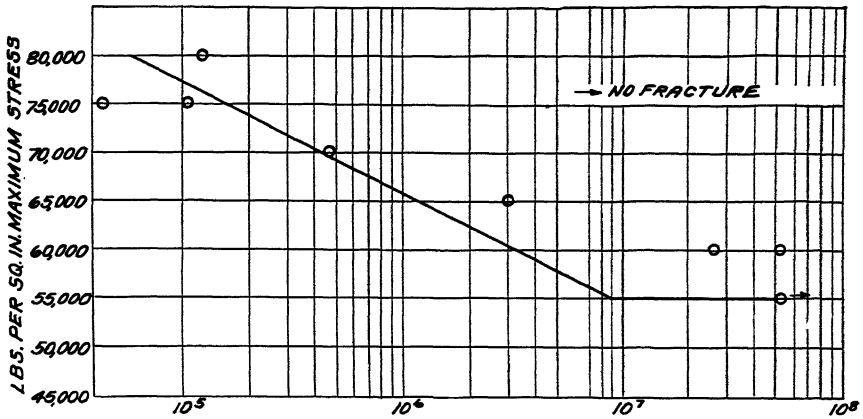
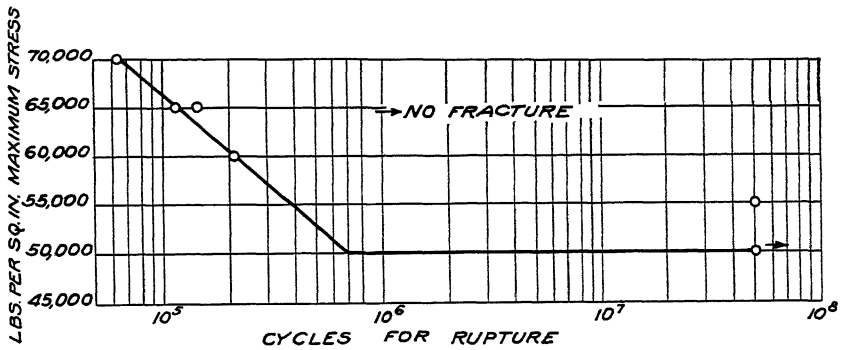FIG. 11.—S-N DIAGRAM FOR NICKEL STEEL B IN STEAM AT 98°C. (208° F.).

FIG. 12.—S-N DIAGRAM FOR NICKEL STEEL B IN 60 LB. STEAM AT 150° TO 160° C
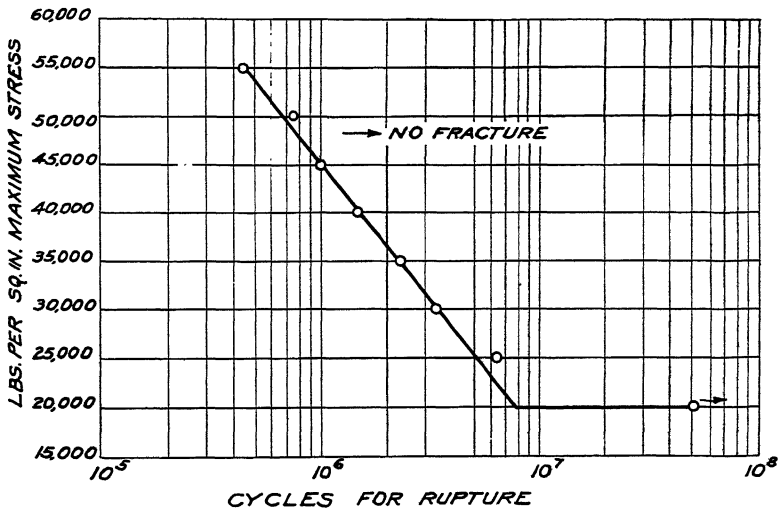(302° TO 320° F.).

FIG. 13.—S-N DIAGRAM FOR NICKEL STEEL B IN THE ATMOSPHERE IN A JET OF STEAM.

The endurance limit of nickel steel B was found to be 55,000 lb. per per. sq. in. at room temperature in the atmosphere, 55,000 lb. per sq. in. in steam at 98° C., and 50,000 lb. per sq. in. in 60 lb. steam at 150° to 160° C.
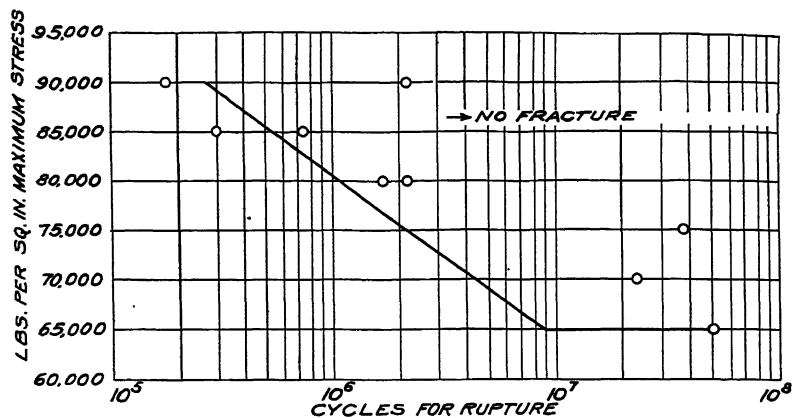

Fig. 14.—S-N DIAGRAM FOR NITRIDED STEEL IN 60 LB. STEAM AT 150° TO 160° C. (302° TO 320° F.).

EFFECT OF OXYGEN

The oxygen content of the steam was determined, 1 kg. showing 0.208 g. of oxygen, which is equivalent to 0.0208 per cent. by weight. This amount is characteristic of a plant not equipped with deaerators.

The effect of condensed moisture and an excess of oxygen was made at once apparent by the series of tests carried out in the atmospheric machine with a jet of steam blowing directly upon the highly stressed portion of the specimens. The endurance limit, under these conditions, of nickel steel B was 20,000 lb. per sq. in. This value is to be compared with that of 55,000 lb. per sq. in. for the series tested at 98° C. in steam containing 0.0208 per cent. oxygen.

NITRIDED STEEL

Specimens of a nitriding steel (typical composition: C, 0.36 per cent.; Mn, 0.51; Si, 0.27; Al, 1.23; Cr, 1.49; Mo, 0.18; S, 0.010; P, 0.013) were heat-treated before machining. They were quenched in oil after heating ½ hr. at 930° C. followed by reheating ½hr. at 650° C. The physical properties after such heat treatment are given in Table 3.

After machining the specimens were nitrided by heating 24 hr. at 500° C. in ammonia gas. The physical properties after this treatment are given in Table 3.

The S-N diagram obtained from specimens of this nitrided material in 60 lb. steam at 150° to 160° C. is shown in Fig. 12. The endurance limit of 65,000 lb. per sq. in. is the highest yet observed in these tests.

TABLE 3.—*Physical Properties of Nitrided Steel Specimen*

Treatment of Specimen	Ult. Str., Lb. per Sq. In.	Yield Pt., Lb. per Sq. In.	Elas. Limit, Lb. per Sq. In.	Elong. in 2 In., Per Cent.	Reduc. of Area, Per Cent.	Charpy Value (Keyhole Notch), Ft.-lb.
Heated ½ hr. at 930° C. Quenched in oil and reheated ½ hr. at 650° C.........	123,000–123,800	97,300–101,500	83,000–86,000	21	62.5–63.3	45.4
Machined and nitrided 24 hr. at 500° C. in NH₃...	122,200–129,900	95,400–106,300		12.5–14.5	29–38	23.2

PROPOSED EXPERIMENTS

As mentioned, the work described in this paper represents the first series of final results. The experiments with nickel steel and the nitriding steel are being continued in steam at higher temperatures and
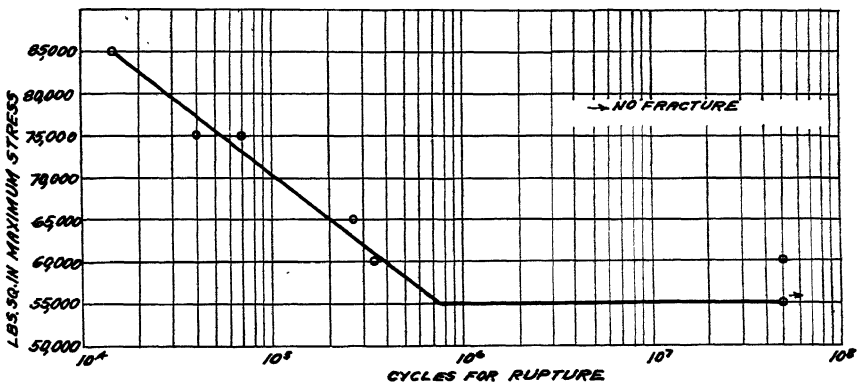

FIG. 15.—S-N DIAGRAM FOR NONCORROSIVE CHROME IRON ALLOY IN 60 LB. STEAM AT 150° TO 160° C. (302° TO 320° F.).

pressures. It is proposed then to study "prior-corrosion fatigue" effects by exposing unstressed specimens in steam for considerable periods of time, after which the endurance properties will be determined under different but controlled conditions.

Work with a noncorrosive chrome-iron alloy containing 12.5 per cent. chromium and 0.10 per cent. carbon is being carried on. Specimens of this material in a heat-treated condition showed the following static physical properties:

Ultimate strength, lb. per sq. in...................... 98,800–105,800
Elastic limit, lb. per sq. in......................... . 59,000– 65,000
Elongation in 2 in., per cent....................... .   23–   28
Reduction of area, per cent....................... .   69–   71
Brinell hardness.................................. ..   207–   228

The endurance limit of this alloy so treated in 60 lb. steam at 150° to 160° C. is 55,000 lb. per sq. in., as shown in Fig. 15.

CONCLUSIONS

The endurance limit of nickel steel, both A and B specimens, has been shown to be lower in 60 lb. steam at 150° to 160° C. than in air at room temperature. The endurance limit of nickel steel B specimens, in the presence of steam, condensed moisture and an excess of oxygen has been shown to be not more than 36.5 per cent. of the endurance limit of similar specimens tested in the atmosphere at room temperature, and in steam containing 0.0208 per cent. oxygen at 98° C.

An endurance limit of 65,000 lb. per sq. in. was obtained in 60 lb. steam at 150° to 160° C. with specimens of a nitrided steel.

DISCUSSION

D. J. McADAM, JR., Annapolis, Md.—Mr. Fuller's paper discusses a phase of corrosion fatigue, the combined influence of stress and corrosion. We have done considerable work at Annapolis on combined stress and corrosion at room temperatures in water with free access of oxygen. There is much need of work such as Mr. Fuller has started. As he says, this is a beginning in investigation of a complicated subject.

It seems to me that some criticism could be made of the way of drawing the stress-cycle graphs. They should represent the stress-cycle relationship; that is, the relationship between the stress and the number of cycles to break. Most of the graphs are not drawn in that way. The curves should be drawn through the points representing the broken specimens. In Fig. 11, for example, three of the points representing breaks are ignored and the line is drawn down below them to a point representing a specimen that did not break. I think that some of the endurance limits are rather low for that reason. However, that does not affect the conclusions in the paper.

The term "endurance limit" as used in this paper has certain disadvantages when it is used to represent the fatigue limit of a corroded specimen. It is better to keep the term "endurance limit" to represent the actual endurance limit of the metal as determined by a smooth specimen, and use the term "fatigue limit" or "corrosion-fatigue limit" for the fatigue limits of other specimens. I found it necessary to do that in some previous papers[3] to avoid confusion.

A distinction should be made between wet steam and dry steam. In the author's experiments the steam used was evidently wet steam. The steam was saturated as it left the boiler, and when it entered the author's apparatus it had cooled enough to permit some condensation of the liquid phase. This introduces a variable which should be taken into account.

[3] D. J. McAdam, Jr.: Corrosion of Metals as Affected by Time and by Cyclic Stress. *Trans.* A. I. M. E., Inst. Met. Div. (1928) 571.

Some Factors Involved in Corrosion and Corrosion-Fatigue of Metals. *Proc.* Amer. Soc. Test. Mats. (1928) **28**, 117.

Corrosion of Metals as Affected by Stress, Time and Number of Cycles. *Trans.* A. I. M. E., Inst. Met. Div. (1929) 56.

Corrosion of Metals under Cyclic Stress. *Proc.* Amer. Soc. Test. Mats. (1929) **29**, 250.

To illustrate the great effect of the liquid phase, I merely refer to some boiler failures which have occurred at Annapolis. The cracks occurred entirely below the water line. That has been found true also in experimental drums in which there was nothing but condensed steam in the lower part of the drum. So that the presence of the liquid phase introduces an important variable.

Then there is the oxygen variable. For the purpose of this paper it is treated as a constant, but it is possible that variation in the small quantity of oxygen may have considerable influence.

In the author's comparison of the effects of steam at 6 lb. pressure and the effects of steam at 15 lb. pressure, if there was an oxygen variable or a water-phase variable some of the observed difference in results would be accounted for.

The effect of time, I think, will have to be considered. The time used was only a few weeks at the longest. It may take a longer time for the effects of corrosion to be apparent. So it is not safe to assume that a fatigue limit has been reached in only 25 days. Doubtless the author has this in mind.

In the author's experiment of allowing steam to strike the specimen in the atmosphere he found a limit of somewhat over 20,000 lb. per square inch. It would be of interest to compare that limit with the limits that we have obtained at Annapolis by running specimens of about the same composition in cold water exposed to air. The author's experiment was made in hot water with access of air, whereas the Annapolis experiments have been made in cold water with access of air. The results obtained with cold water are about the same as the author's results. The effect of water temperature, therefore, seems to be small. Possibly, however, variation in the quantity of water offset the effect of the difference of temperature.

In December, 1926, G. D. Lehmann,[4] in England, ran some specimens in distilled water without air and found that there was no lowering of the endurance limit. This illustrates the necessity of considering the two variables. The effect of air without water is practically the same as the effect of water without air.

F. N. SPELLER, Pittsburgh, Pa.—Mr. Fuller's evidence as to the effect of corrosion-fatigue ties in fairly well with other data on this subject. For instance, the laboratory of applied science at the Massachusetts Institute of Technology made some fatigue tests (unpublished) with a jet of high-velocity moist air playing on the sample under stress. The results indicated about the same fatigue value of this material as was previously found in a stream of tap water.

A. M. Binney,[5] in England, recently published some similar tests made with salt water carrying a variable amount of oxygen. In one of these tests, he replaced most of the oxygen with hydrogen and found a marked rise in the fatigue limit; so, in short, it may be said that as evidence accumulates, it becomes clearer that the factors that govern ordinary corrosion also control the effect of corrosion and stress combined.

It would seem highly desirable to run some tests with air-free steam in the well designed apparatus that Mr. Fuller has used for his tests. Such steam can be obtained from a modern steam plant using an efficient deaerator. He has shown that with a relatively small amount of oxygen in the steam, the corrosion-fatigue limit is not very far below the air limit, but with a large amount of oxygen, under the same conditions, the metal fails at a much lower stress. It would seem, therefore, that if the oxygen were entirely removed, the damage due to the corrosion might be practically elimi-

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[4] G. D. Lehmann: Variation in the Fatigue Strength of Metals when Tested in the Presence of Different Liquids. Aeronautical Research Committee (British), December, 1926.

[5] A. M. Binney: The Influence of Oxygen on Corrosion Fatigue. *Engineering* (1929) **128**, 190, 191.

nated.   This would seem to be an important consideration in the maintenance of steam turbines.

T. S. FULLER.—It is difficult to carry on such an investigation as has been described. Frequent repairs to the machines, especially to the bearings on the loaded ends of the specimens, are necessary.   All experiments described in this paper have been made in steam, shown by the entropy diagram to contain a small percentage of moisture.   It is my opinion, however, that the amount of liquid phase present, in all except the experiment of the steam jet in air, is so small as to be relatively unimportant.   The specimens remain surprisingly bright after an exposure of three weeks.

In experiments which have been carried on since the manuscript for this paper was prepared, the endurance limit of nickel steel A in a steam jet in the atmosphere has been found to be 20,000 lb. per square inch.   This is the same value obtained with nickel steel B under similar conditions, indicating that under severe conditions of corrosion the initial physical properties of the steel are not important.

G. B. WATERHOUSE, Cambridge, Mass.—May I ask the analysis of both?

T. S. FULLER.—Both nickel steels A and B were of the type containing 3.5 per cent. nickel and 0.35 carbon.   The difference in physical properties was due to difference in heat treatment.

Development of Casing for Deep Wells; a Study of Structural Alloy Steels

BY F. W. BREMMER,* AMBRIDGE, PA.

THE drilling of constantly deeper oil wells has made it imperative that the manufacturer of casing be ever searching for new methods and new materials to meet the increased demands. One phase of this search constitutes the subject matter of the present paper.

Starting from the original Drake well in 1859, the depth of wells has advanced by leaps and bounds, until today depths of 6000 to 8000 ft. are common. Conditions point to the necessity for drilling to greater depths, and it is not at all improbable that much of the future oil produc-
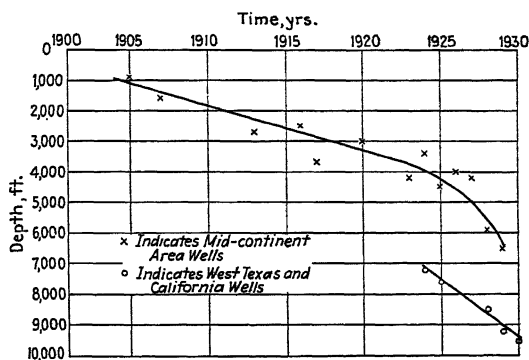

FIG. 1.—TREND IN DEPTH OF OIL WELLS.

tion will be from wells around 10,000 ft. deep. The trend to deeper wells is nicely illustrated by the curve in Fig. 1.[1] The points plotted are the maximum depths attained in the various pools which were at their peak for the years given.

It may be of some interest to observe the change that has taken place in the tensile and collapsing stresses over the last 25 years. The pressure at the bottom of a 900-ft. hole, equivalent to the pressure caused by an equal column of water, is only 450 lb. per sq. in. The equivalent water pressure corresponding to the depth of the deepest hole today would be 4762 lb. per sq. inch.

The tensile stresses in the top joint due to the weight of the casing string also has increased enormously during the same period. For example, the unit stress (at the root of the first perfect thread), in the top joint of a string of 5¾-in., 22.5 lb. per ft. casing is only 4050 lb. per sq. in. for the well of 25 years ago. The stress in the top joint of the present deepest hole, assuming the same size casing was used for the inner string, would be 42,360 lb. per sq. inch.

First wrought-iron, and then mild-steel, lap-welded casing provided sufficient strength for the tensile and collapsing stresses encountered. Between 1920 and 1925, with the advent of 3000-ft. wells, the necessity for a stronger casing became evident. Steel higher in carbon, adapted to manufacture into casing by the seamless process, offered the requisite physical characteristics. Accordingly, seamless steel casing continued to satisfy the requirements until early in 1929. Again, demand arose for a stronger casing, one capable of being set at depths approaching 10,000 ft. This demand necessitated the development of a steel to meet the increased requirements and resulted in the addition of grade D—high tensile casing—to the A.P.I. specifications for the physical properties of seamless casing (Table 1.)

TABLE 1.—*American Petroleum Institute Specifications for Physical Properties of Casing Material, Minimum Requirements*

Grade[a]	Tensile Strength, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Elongation in 2 In., Per Cent.
A (0.10–0.20 C)	48,000	30,000	40
B (0.30–0.40 C)	70,000	40,000	25
C (0.40–0.50 C)	75,000	45,000	20
D (Alloys of various types)	95,000	55,000	18
E[b] (Alloys of various types)	110,000	60 per cent. of Tensile Strength	

[a] The notes in parentheses indicate the type of material that will give the required properties.

[b] Grade E is tentative at present.

FACTORS INVOLVED IN SELECTING CASING FOR DEEP WELLS

There are two primary objects in casing a well:

1. To prevent water and cavings from entering the hole and interfering with drilling to the proper depth.

2. To provide a permanent wall for the hole drilled, so that any oil or gas found can be controlled.

To satisfactorily attain these objectives, three factors of vital importance must be considered in the selection of casing for the modern deep well:

1. The strength of the string of casing joints in tension.

2. The resistance of the string of casing joints to external collapsing pressure.

3. The toughness or resistance of the string to shock.

The strength of casing joints in tension is a function of several variables. Those of prime importance are: (1) the yield point of the casing steel; (2) diameter and wall thickness of casing; (3) design of the threaded joint. Similarly, resistance to collapse by external pressure is affected by a number of different factors, of which the principal ones are: (1) the yield point of the casing steel; (2) diameter and wall thickness of casing; (3) original departure of casing cross-section from a perfect circle (out-of-roundness).

The benefits to be derived from high-strength casing should be readily apparent. Whenever a string of casing is raised in a well, the top joints must bear not only the weight of the entire string but also the load necessary to overcome friction of the pipe in the hole. In shallow wells the load caused by friction may be negligible, but in deep wells the additional load might be sufficient to cause failure. High tensile casing offers a greater margin of strength to overbalance the frictional load and is therefore particularly valuable for the deeper wells.

The advantages of high-strength casing are equally important in resisting collapsing pressures. The greatest danger of collapse exists when the string is placed in tension. The resulting tensile stress in the metal diminishes the collapsing resistance of the casing in almost direct proportion of this stress to the elastic limit of the steel. Consequently, a string of casing that is entirely safe under ordinary conditions may be in imminent danger of collapse when subjected to a severe pull.

Toughness is an essential item in the make-up of satisfactory casing. Considerable shock is received from the movement of the rotary stem in drilling and sometimes there is impact from caving formations. Instances are known where casing has snapped off, even after cementing, and the fracture has had the appearance of a break due to impact stress. Therefore the transverse strength, ductility and toughness must be carefully considered in the selection of casing for deep wells.

The sizes of casing and the design of joints are fairly well standardized at present and may be disregarded in this discussion. Attention will be given only to the steel of which the casing is made, and its importance in determining the resistance of the string to tensile, collapsing and impact stresses.

SELECTION OF STEEL FOR DEEP-WELL CASING

The large amount of hot work necessary in piercing and rolling casing by the seamless method refines the grain to a great degree. Cooling from the finishing temperature progresses rapidly, on account of the thin

section and tubular shape.   These two influences tend to make the effects of alloy additions more pronounced than in solid sections.

Two expedients for increasing the physical properties of steel structure are open:

1. Select an analysis that will give the desired strength in the as-rolled condition.

2. Thermally treat the rolled product in a way that will produce the desired strength.

Several requirements and conditions limit the extent to which these methods may be carried.   The casing steel (1) evidently must have the quality to withstand piercing and rolling into a seamless tube; (2) must have sufficient ductility and shock resistance in the finished tube to allow straightening; (3) must be of a hardness that will permit cutting off and threading in the regular commercial automatic machines.

The question of the cost of producing a high-strength casing must be considered in view of the large tonnages required in deep wells. An idea of the amount of casing used can be gained from certain California wells.   Here, at depths of only 3600 to 4000 ft., approximately 200 tons were needed.   Accordingly, a modern deep well of about 8500 ft. requires about 675 tons of casing, representing a correspondingly big item of expense in the cost of the well.·

Thermal treatment of casing to improve strength offers a number of possibilities, that is, (1) normalizing; (2) air hardening followed by drawing; (3) liquid quench followed by drawing.

As is well known, certain steels develop improved properties on reheating after rolling followed by cooling in still air.   This method is feasibly applied to casing.   Tubes can be heated easily in simple furnaces and production maintained without an unreasonably large outlay for equipment.   Warpage is a factor that may be controlled by proper design of the cooling-bed arrangement.   A combination of an air quench with a tempering treatment offers distinct merit as a means of increasing strength for certain classes of steel.   The resulting properties are capable of being controlled and maintained with a high degree of uniformity. This process would not be so attractive from the standpoint of obtaining large production with minimum facilities.

A liquid quenching treatment followed by a draw usually develops the maximum properties of a steel.   This is definitely proved by the success that has been achieved by heat-treated drill pipe.

EXPERIMENTAL WORK

Six different types of steel were selected as being suitable for deep-well casing. A 6-ton heat of each was made in an electric furnace.   The electric furnace was used to reduce steelmaking variables and supply small heats for the tests.

The composition of each of the steels studied is shown in Table 2. The designations appearing in the first column will be followed throughout the course of the paper.

TABLE 2.—*Composition of Steels Studied*

Designation	C, Per Cent.	Mn, Per Cent.	Si, Per Cent.	Cr, Per Cent.	Ni, Per Cent.	Mo, Per Cent.
2½ Mn[a]...............	0.19	2.65				
1¾ MnMo.............	0.27	1.71				0.25
SiMn[b]................	0.33	1.17	1.10			
SiMnCr[b]..............	0.31	1.13	0.87	0.42		
1¾ NiMo.............	0.30				1.73	0.25
CrMo................	0.31			0.58		0.22

[a] V. N. Krivobok, B. M. Larsen, W. B. Skinkle and W. C. Masters: Some Characteristics of Low-carbon Manganese Steel. *Trans.* A. I. M. E. (1927) **75**, 404.

[b] A. B. Kinzel: Silicon-Manganese Steels with Chromium Additions for Engineering Applications. *Trans.* Amer. Soc. Steel Treat. (1928) **14**, 866.

Each heat was processed into 6⅝-in. by 24 lb. per ft. A. P. I. casing (6⅝ in. O.D. by 0.352-in. wall) in the regular manner for making seamless tubes. All of the steels were easily pierced and rolled. The 2½ Mn steel, however, was brittle in the as-rolled condition, as evidenced by the breaking of several lengths in the rotary straightening operation. This steel, also, was very difficult to cut on the automatic cut-off machines used in cropping the ends.

All treating and testing was done under conditions as nearly the same as possible, so that the results should be fairly comparable.

Tensile samples consisted of 1½ by 12-in. longitudinal strips cut from the tube wall. Impact samples were obtained by upsetting the ends of the pipe to a wall thickness that would permit cutting the standard square Izod, V-notch, impact specimen.

Normalized samples were held at temperature for ½ hr. followed by cooling in still air.

Heat-treated samples were held at the quenching temperatures for ½ hr. and then immersed in water for 5 min. The quenching temperatures used are considered the optimum for each steel and were determined by experiment or from published data. The temperature of the water was maintained at 125° F. Quenched pieces were tempered immediately for 1½ hr., followed by air cooling. Impact samples of each type of steel were also water-cooled from the 1100° F. drawing temperature to determine whether any were subject to temper brittleness.

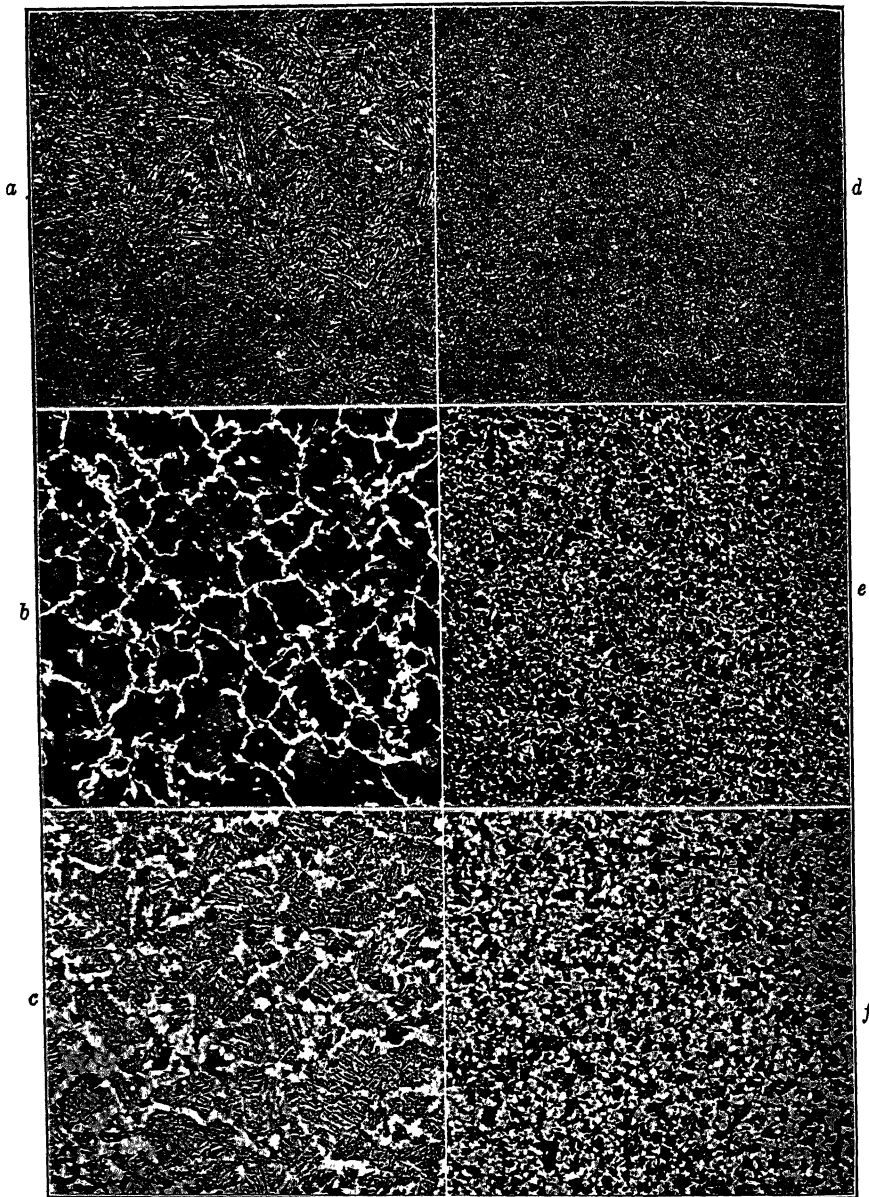The treated impact samples were tested for cracks by first magnetizing

FIG. 2.—MICROSTRUCTURE OF STEELS IN
AS-ROLLED CONDITION.   × 100.
  a. 1¾ MnMo.
  b. SiMnCr.
  c. CrMo.

FIG. 3.—MICROSTRUCTURE OF STEELS IN
NORMALIZED CONDITION.   × 100.
  d. 1¾ MnMo.
  e. SiMnCr.
  f. CrMo.

Longitudinal sections.   Samples etched with 5 per cent. nital.

and then dusting with whitened, powdered, highly permeable iron. Cracks not visible to the naked eye were detected by this method.

All test figures are the average of at least two determinations, and for impact values, the results are the average of at least six tests.

Table 3 gives the results of the mechanical properties obtained in testing the six experimental steels in the several conditions. Included in the tabulation are the A. P. I. specifications for grade C and grade D casings.

Metallographic examination of the six steels in the various conditions was made to correlate microstructure with mechanical properties. Many photomicrographs have been taken, but it would be impractical to reproduce all of them here. Only a few of the most representative are shown in Figs. 2 and 3.

DISCUSSION OF EXPERIMENTAL RESULTS

It should be understood that the foregoing data are of value for comparative purposes only. However, the results reported for the steels in the as-rolled condition are indicative of regular mill practice.

As-rolled Condition

An examination of the physical properties of the six steels in the as-rolled condition reveals several interesting facts. The yield point and ultimate strength of each is well able to meet the grade D, A. P. I. specification. However, this is at the expense of ductility and machinability in the two alloys 2½ Mn and 1¾ MnMo. No figures are presented on the notched-bar impact value of the steels in the as-rolled condition, but there is reason to believe that 2½ Mn and 1¾ MnMo are rather poor in this respect. As mentioned, several pieces of the 2½ Mn casing broke in being straightened on the rotary straightening machine. The pseudomartensitic appearance of the microstructure of the 2½ and 1¾ MnMo (Fig. 2a) steels in the as-rolled condition is also an indication of a brittle tendency. It was impossible to thread 2½ Mn casing (as rolled) with the regular automatic machines. The 1¾ MnMo casing threaded with difficulty.

The 1¾ NiMo and the CrMo steels are handicapped at the start by their high cost. Nickel and molybdenum are among the more expensive alloys that are added to steel. These two types of steel revealed a desirable combination of strength, ductility, toughness and machinability.

The SiMn and SiMnCr alloys gave casing with good yield point and ultimate strength; the yield point of the SiMnCr steel was markedly high. The ductility and hardness remained at a very satisfactory point in these two steels.

TABLE 3.—*Physical Properties of Experimental Steels*

Type Steel	Heat Treatment, Deg. F.	Yield Point, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.	Brinell Hardness, 3000 Kg.	Izod V-notch Ft-lb. Air	Water
Grade C, minimum.		45,000	75,000	20				
Grade D, minimum.		55,000	95,000	18				
2½ Mn								
As rolled........		a	134,200	13.6	25.4	269–293		
Normalized......	1,700	a	148,500	14.0	20.6	293–302	5.5	
Heat treated.....	1,700– 900	129,400	144,500	17.9	42.2	302–311		
	1,700–1,000	125,000	134,400	19.5	38.9	286–286	5b	
	1,700–1,100	112,500	124,500	21.6	45.2	269–272	9.3b	24.3a
	1,700–1,200	96,200	107,600	26.6	49.2	235–241	73b	
1¾ MnMo								
As rolled........		78,000	120,100	18.9	37.2	255–255		
Normalized......	1,600	88,000	127,100	20.5	32.5	262–269	27.5	
Heat treated.....	1,550– 900	142,400	160,500	16.4	39.0	332–340		
	1,550–1,000	132,100	149,200	18.0	38.4	311–321	47	
	1,550–1,100	119,300	136,000	20.5	42.8	286–293	52.5	55.3a
	1,550–1,200	106,300	118,800	24.6	47.8	248–255	63.5b	
SiMn								
As rolled........		60,100	111,600	25.4	42.1	217–217		
Normalized......	1,650	76,200	109,400	29.6	54.1	212–217	45.5	
Heat treated.....	1,650– 900	131,700	153,300	17.7	35.8	293–311		
	1,650–1,000	131,400	143,700	19.3	40.0	293–302	42	
	1,650–1,100	113,500	128,200	22.2	44.9	269–269	48.7	51.3
	1,650–1,200	101,700	113,800	25.8	47.8	241–255	66	
SiMnCr								
As rolled........		72,300	117,400	22.7	43.0	228–241		
Normalized......	1,650	75,600	110,500	29.5	49.3	217–217	49.7	
Heat treated.....	1,650– 900	142,700	161,000	16.7	37.1	332–340		
	1,650–1,000	138,300	148,400	19.3	40.4	302–311	41	
	1,650–1,100	120,000	134,000	21.1	46.1	277–286	54.5	52.6
	1,650–1,200	106,900	122,300	24.6	47.2	255–255	71	
1¾ NiMo								
As rolled........		78,100	103,900	22.5	41.1	214–223		
Normalized......	1,650	75,800	101,800	23.9	49.1	217–223	56.3	
Heat treated.....	1,550– 900	143,700	158,700	16.5	33.5	321–332		
	1,550–1,000	134,100	143,100	18.7	44.1	302–302	51	
	1,550–1,100	115,800	127,600	20.9	47.1	269–277	62.3	56.3
	1,550–1,200	103,400	112,500	26.9	50.6	235–241	69.8	
CrMo								
As rolled........		72,700	102,200	22.0	44.4	207–228		
Normalized.... .	1,650	66,000	95,700	28.6	45.6	196–207	49.1	
Heat treated.....	1,600– 900	150,900	163,500	15.6	38.1	302–351		
	1,600–1,000	134,900	149,800	19.5	44.1	311–321	47	
	1,600–1,100	119,400	129,200	21.2	47.7	262–267	52.7	· 54.6
	1,600–1,200	102,400	114,800	23.8	49.9	241–248	74.3	

a No definite yield point observed; yield point close to ultimate strength.
b These samples were cracked after heat treatment.

From the data obtained it seemed as though a steel of the SiMn or SiMnCr type, as rolled, would offer one solution to the problem of providing suitable casing for the deeper wells.

Normalized Condition

The properties on normalizing are considerably changed from those as rolled. The 2½ Mn and 1¾ MnMo steels exhibited an appreciable tendency towards air hardening. The remainder showed some small degree of softening. The best results that were secured by normalizing were found in the SiMn, SiMnCr, and 1¾ MnMo types. The elastic ratio (ratio of yield point to ultimate strength) and ductility were considerably improved while still maintaining satisfactory hardness and good impact value.

The susceptibility of the 2½ Mn steel to air hardening is well illustrated by the test figures in Table 3. The impact value of this steel after normalizing was very low, indicating marked brittleness. The 1¾ MnMo steel gave high tensile properties with only fair ductility. Also, the shock resistance was of a much lower order than that of the other alloys (excepting 2½ Mn).

It is realized that comparison on the basis of yield point is not exactly fair in the case of the 1¾ MnMo alloy. This steel should have been tempered after normalizing to obtain a yield point of 75,000 lb. per sq. in.; then the other properties would be strictly comparable. However, it is believed that the relative nature of the conclusions drawn would not be affected even had tempering been done.

Heat-treated Condition

As would be expected, quenching and tempering of the six steels resulted in vastly increased mechanical properties. The test figures give an idea of the maximum properties that can be developed in each type of steel after simple heat treatment under the given conditions.

A critical examination of the properties developed by quenching and then tempering at 1100° F. shows that the tensile properties of the six steels are practically the same, and the Brinell hardness does not vary widely. In the matter of shock resistance, as determined by the Izod notched-bar impact test, larger differences are noted. The 2½ Mn steel gave low impact values, which would be decidedly dangerous in deep-well casing. The values for the other steels were good and indicated satisfactory toughness.

The experiment performed to determine whether the steels were subject to temper brittleness was too incomplete for general conclusions to be drawn. The results seemed to indicate that the 2½ Mn alloy was liable to the phenomenon. No discussion of this much debated question will be attempted here.

The liability of a steel to warp and crack in quenching determines to a large degree the suitability of that steel for a heat-treated structure, such as seamless tubing. The results of the magnetic inspection of the

heat-treated samples showed that two steels, 2½ Mn and 1¾ MnMo, were not exempt from cracking caused by quenching. This behavior precludes their employment in heat-treated casing where freedom from leaks is essential. Warpage in heat-treating casing would be difficult to learn by experiments on small test pieces, therefore full sections were completed and quenched and the warpage qualitatively observed. Results were closely in line with those predicted by dilatometer measurements on various similar steels at the Union Carbon and Carbide Research Laboratories, in which SiMnCr steels were the most favorable in this respect.

Metallography

The microstructures exhibited in Figs. 2 and 3 show good correlation with the physical characteristics reported in Table 3. There is little need for discussion of the photomicrographs except to point out the refinement of grain brought about by normalizing. The structures developed by water quenching and tempering were uniformly fine for the six steels. No appreciable differences between them could be observed, to warrant including photomicrographs in this discussion.

COMMERCIAL DEVELOPMENT

At this point, the problem was to select a relatively cheap steel suitable for deep-well casing and, if possible, also suitable for use in other seamless tubular goods, probably in a treated condition. Based on the data obtained, it is evident that a steel of the SiMnCr type offers the most logical solution of the steels tested.

Many open-hearth heats of different analyses (SiMnCr type) were rolled into commercial casing to study their behavior in the mill. This study showed that a steel with relatively high alloy content (similar to the small heat described in the preliminary experimental work) was capable of meeting grade E requirements. Furthermore, a steel with a lower alloy content sufficed for grade D specifications.

In both grade D and grade E analyses the SiMnCr steels showed excellent working properties and marked freedom from steelmaking difficulties. Accordingly, grade D casing is made from the following analysis, modified somewhat for various diameters and wall thicknesses: C, 0.40 per cent.; Mn, 1.10; Si, 0.25; P and S, 0.40 max.; Cr, 0.18. Seamless couplings of the same material are regularly furnished on grade D casing.

A large amount of testing has been done on the commercial sizes of this casing to insure its having the requisite properties. Two strip tensile tests have been made on every heat rolled. Table 4 gives the results of a number of such tests compared with figures obtained on the less

strong (0.40 to 0.50 per cent. carbon) grade C material. The data have been obtained on a range of sizes from 5 in. by 15 lb. per ft. to 13⅜ in. by 68 lb. per ft. casing.

TABLE 4.—*Comparison of Physical Properties of Grade C and Grade D Casings*

A. P. I. Grade	Number of Tests	Yield Point, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.
C	Avg. 340	53,000	98,000	25	39.5
	Range	47–58,000	89–105,000	20–30	32–47
D	Avg. 200	64,750	107,500	25	43
	Range	58–69,000	98–112,000	18–28	35–50

A detailed study of the strength of full-sized casing joints is now in progress. This work includes a study of the various factors in joint design which influence strength, and will be made the subject of a future paper. A brief comparison of the tensile strengths of grade C and grade D casing joints is available from the data so far obtained (Table 5).

TABLE 5.—*Comparison of Tensile Strength of Grade C and Grade D Casings Tested in Full Section*

A. P. I. Grade	Type Steel	Size Tested[a]	Wall Thickness	Ultimate Strength at Failure, Joint-lb.	Pipe at Gage Point, Lb. per Sq. In.	Ultimate Strength Strip, Lb. per Sq. In.
C	0.40–0.50 C		0.343	409,000	80,000	95,250
C	0.40–0.50 C		0.343	411,000	80,200	95,900
C	0.40–0.50 C	6⅝ In. 24 Lb. per Ft.	0.344	410,000	79,600	94,650
D	SiMnCr		0.324	495,000	103,700	107,500
D	SiMnCr		0.327	568,000	117,800	106,000
D	SiMnCr		0.335	491,000	98,800	106,850

[a] 10 thread, ⅜ in. taper, 3 in. total length of thread.

The data in Table 5 indicate that the strength of the joint has not only been raised by the use of SiMnCr steel, but that it has been increased in a greater ratio than the increase in ultimate strength. In other words, a higher joint efficiency has been obtained by using SiMnCr steel.

There is no standard transverse test applicable to pipe samples. Accordingly, simple shop methods were devised to test the characteristics of the grade D casing in a transverse direction. Rings, approximately 2 in. wide, were cut from the ends of a number of pieces of grade D casing,

for which the physical properties were known.   Each ring was flattened in a press until rupture just started.   At this instant, crushing was stopped and the height of the flattened ring was measured.   This information indicated that the height after crushing represented six to eight times the wall thickness of the casing.   As a result, it was decided that a ring possessed satisfactory transverse ductility and toughness if it could be crushed to a height of 10 times the wall thickness *without rupture,* and therefore this method is used as a routine part of the inspection of grade D casing.   The crop ends from every tube are flattened in a large press to a distance of 10 times the wall thickness of the casing (Fig. 4).
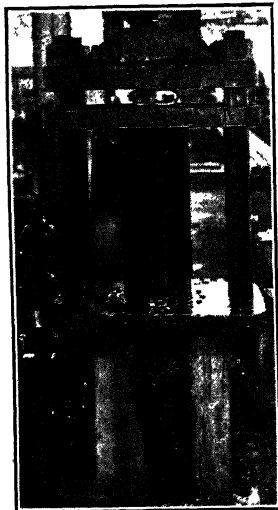
FIG. 4.—FLATTENING A CROP END.

Tubes that fail in the flattening test are normalized and retested.   The percentage of tubes requiring normalizing is very small, only a fraction of one per cent.   Occasionally a tube is finished at a lower temperature by the seamless mill.   Any cold work received accounts for the failure to pass the test.   Normalizing has always restored the ductility, enabling a ring to pass the flattening test satisfactorily.

Fig. 5 shows rings from several sizes of grade D casing, SiMnCr type, which have been flattened by blows from a steam hammer.   Here again, the ductility and shock resistance of this casing has been well illustrated.

FIG. 5.—RINGS FROM GRADE D CASING FLATTENED UNDER A STEAM HAMMER.

	Original Diameter, In.	Weight, Lb. per Ft.	Wall Thickness, In.	Height after Flattening, In.	Brinell Hardness
Left.............	7	28	0.393	$2\frac{3}{4}$	248
	7	24 .	0.332	3	228
	$9\frac{5}{8}$	40	0.391	$3\frac{9}{16}$	241
	$9\frac{5}{8}$	40	0.391	$3\frac{3}{4}$	248
	$13\frac{3}{8}$	68	0.480	$4\frac{1}{16}$	235
Right............	$13\frac{3}{8}$	68	0.480	$4\frac{3}{8}$	228

Another shop test, which has been performed on full-sized lengths of SiMnCr casing, is shown in Fig. 6.   This is a photograph of a piece

of grade D casing of 7-in. O.D., 24 lb. per. ft. and Brinell hardness 229.
Flattening has been carried to a distance of $3\frac{1}{8}$ in. in two places at right
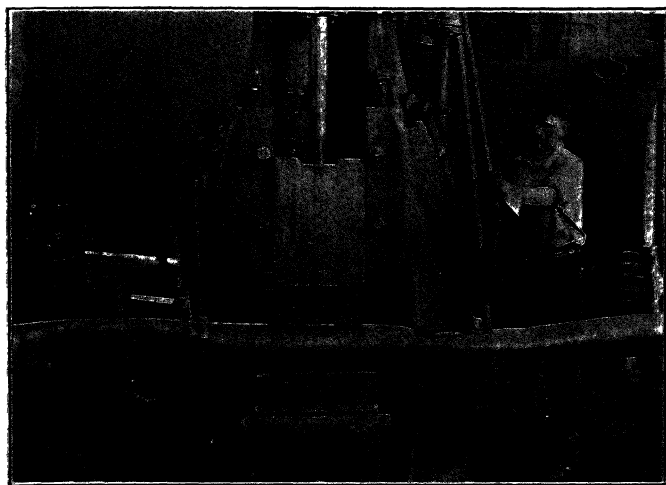angles to each other.   Moreover, there has been no indication of rupture

FIG. 6.—TRANSVERSE DUCTILITY OF GRADE D CASING.   7 IN. O.D., 24 LB. PER FT.
228 BRINELL HARDNESS.

of the surface at any point.   It is believed that the transverse ductility
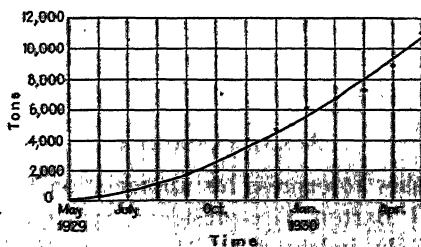and shock resistance of SiMnCr type grade D casing can not be proved in
a more convincing manner.

FIG. 7.—CUMULATIVE MONTHLY TONNAGE SHIPMENTS OF GRADE D CASING.

Some of the depths to which SiMnCr type of casing has been set
are given in Table 6.

Anticipating future demand, work has been done on the development
of casing to meet grade E requirements.

Several experimental heats rolled into $6\frac{5}{8}$-in. and $9\frac{5}{8}$-in. casing have
developed the required tensile properties.   The following analysis has
proved satisfactory for the grade E specification, being slightly modified
for different sizes and weights: C, 0.40 per cent.; Mn, 1.10; Si, 0.85; P and
S, 0.040 max.; Cr, 0.50.

TABLE 6.—*Depths to Which SiMnCr Casing Has Been Set*

	Outside Diameter, In.	Lb. per Ft.	Depth, Ft.
Reagan County, Texas............	6⅝	28	8000
	5½	20	7950
	5	18	7806
California and Oklahoma..........	11¾	60	4800
	10¾	45	6480
	9⅜	40	5914
	9	45	6459
	8⅝	36	7500

A brief summary of physical test results is given in Table 7.

TABLE 7.—*Physical Properties, Grade E Casing*

	As Rolled	Normalized
Yield point, lb. per sq. in..................	68–80,000	70–80,000
Ultimate strength, lb. per sq. in.............	118–138,000	115–130,000
Elongation in 2 in., per cent................	17–24	18–25
Reduction in area, per cent.................	30–40	35–45
Brinell hardness..........................	269–285	248–277

These figures are not to be construed as indicative of practice to be followed in the future.

That SiMnCr type grade D casing is fulfilling a definite need is apparent from the fact that over 2,000,000 ft. have been shipped. Fig. 7, showing the cumulative monthly tonnage shipments of grade D casing, illustrates the increasing demand for this type of product.

ACKNOWLEDGMENT

The author wishes to express his appreciation for the kind interest shown by Mr. C. R. Barton, Vice-president, Spang, Chalfant & Co., Inc. He is also especially indebted to Mr. A. V. de Forest, consulting metallurgist, for the great amount of help and encouragement given in the preparation of this paper. The author thanks A. G. Sturrock for assistance in the metallographic work, and Mr. F. H. Bremmer for help in obtaining physical test data.

DISCUSSION

C. H. HERTY, JR., Pittsburgh, Pa.—How is this particular grade of steel made?

F. W. BREMMER.—We do not make the steel ourselves but we are in close touch with the manufacturer who does make it. It is made in a 100-ton open-hearth furnace, with considerable attention to open-hearth practice. As you know, in the manufacture of a seamless tube, the piercing operation, especially, tends to open up

any slight defect that is in the material. Steel for seamless tubes must be of an exceptionally high quality; that is, the forging grade as described in the paper. So I think I can say that a practice very closely approximating that of forging-steel practice is used in making this type of steel. As to the actual details and working heats, I do not have any information.

C. E. WILLIAMS, Columbus, Ohio.—I have had no experience with this kind of steel, but evidently it has some important commercial applications. Evidently there is little difference in the physical properties of grade E casing in the as-rolled and normalized conditions. Is this steel normalized in practice, and if so, why?

F. W. BREMMER.—It is not our practice to normalize. Normalizing the large quantities we use would be a difficult manufacturing problem. We have rolled, I would say, about 30,000 tons since we started. We make between 1000 and 1200 tons in 24 hr., and to normalize that would require a large amount of furnace capacity. We are able to get required physical properties in the as-rolled condition. It is to our advantage, as long as it is consistent with required physical properties, to furnish material in the as-rolled condition.

C. H. HERTY, JR.—Do you know what yield you get out of the ingot on that practice?

F. W. BREMMER.—I do not know the yield at the open-hearth plant, but I do know the yields that we get in the rolling of this material. It compares very favorably with our standard 40 to 50 carbon material in which the round, as charged into the hot mill furnace, as compared with the tube as cut off, yields around 90 or 92 per cent., depending on the size we are rolling.

C. H. HERTY, JR.—Do you know about the yield from the ingot?

F. W. BREMMER.—I do not know. I venture to say it is the same as that obtained from the 40 or 50 carbon material.

C. H. HERTY, JR.—That 40 to 50 is not as high silicon?

F. W. BREMMER.—No.

A. B. KINZEL, New York, N. Y.—In this particular steel, Dr. Herty, the high silicon does not seriously affect the yield because of the balance of the silicon, the chromium and the manganese which it contains.

This silicon-manganese-chromium steel was originally worked out in its experimental phases at the Union Carbide and Carbon Research Laboratories. As Mr. Bremmer says, we published the results of our work about two years ago. Mr. Bremmer took our laboratory results and tested them on a production job.

We started out on this field with the idea that the physical properties of most alloy steels as heat-treated are very similar; that is, one alloy steel is not selected for a given job rather than some other alloy steel because of the physical properties in a limited number of test pieces. We can get the same ductility and strength ratio in a dozen different alloy steels. That led us to the generalization that with a moderate alloy quantity and proper handling, all alloy steels in a given range (and I am speaking now of the structural and engineering range such as the S. A. E.) could be made to give the same general physical properties depending on the mass. What determines the choice of steel if this generalization is even approximately true? Four things: ease of manufacture; uniformity of results, and ability to reproduce without special heat treatments and last, but foremost, the cost. So we started out using the three least expensive alloys commonly used in steelmaking. We proceeded to make a great

many heats and finally determined the analysis giving the heat balance of properties. We found one very extraordinary thing which probably contributed materially to the commercial success of the steel; with this combination of elements (this was apparent even in the small scale 300-lb. heats with which we were working), the difficulties due to ingotism were greatly reduced.

We all know the difficulties involved in making the steels with 1 per cent. silicon and 1 per cent. manganese. However the straight manganese steels are good. They have much usefulness, and they are improved by the addition of chromium. We have also made some laboratory observations on the chrome-silicon combination with the same indications.

So, on putting the three elements together, they worked as we expected them to, and resulted in a satisfactory condition on freezing. The net result is that ingot troubles are greatly reduced because of this combination.

The next point we had in mind was that heat-treating is an expensive operation Any steel to be used on a tonnage basis can be heat-treated if the service warrants it, but in general it is not warranted in large sections.

Therefore we started out on a different angle, and investigated the effect of the various alloys on the properties as rolled and as normalized. We found that the difference between as rolled and as normalized was very small indeed with the SiMn-Cr steels. That is why it is possible to run these tubes through the mill as rolled. It is not necessary to treat them, in spite of the alloy content. I might say that the shock resistance checks up with the other values quoted here.

There is another interesting point in the paper that I might bring out; namely, the matter of warpage in heat treatment. I have just been talking about as-rolled steels. That is one problem. If heat-treated material be used, then the problem of warpage presents itself. From purely theoretical consideration, it was decided that warpage might be predicted by measuring the difference in temperature reduction of the critical points in two rates of cooling, one cooled in the furnace and one cooled in still air. We found that on this steel we got a drop of about 38° in the air-cooled over the furnace-cooled material. We were using the Rockwell type dilatometer. Other steels that we were working with, including the chrome-molybdenum, chrome-nickel, and a great many others, all showed greater differences. I will not go into the theory of why we believe this to be a measure of the tendency to warp. The interesting part is that work on full size samples, which Messrs. Bremmer and de Forest very kindly reported to me, substantiated that theory.

A. V. DE FOREST, Bridgeport, Conn.—This work has been pretty well covered by Mr. Kinzel. We have really set out here to try and apply alloy structural steels to a definite problem. The problem was to select the cheapest and the most economical steel to get such desirable mechanical properties. In the course of the comparison, we covered a considerable range of structural possibilities and came to the conclusion (thanks to Mr. Kinzel and his laboratory) that it was possible to get an alloy steel that would do in the as-rolled condition what most of the possibilities would do only in a normalized condition. It is very pleasing to have been able to take laboratory results and place them in practice right away. That does not often happen; I wish it did.

But this particular kind of investigation is, I think, the type that will have to extend to all fields where there is a close competition between cost and desirable features. It is necessary to look over all the possibilities in order to balance up just what is available in commercial quantities as well as in laboratories.

One of the points of interest here, which is not often met with, is that the transverse properties are the important ones. In this case, as we saw from the bending test, we are really interested in properties at right angles to the direction of rolling.

Normally, steels are tested only in the direction of rolling. In many of our results we have steels that are identical in the direction of rolling but are far superior, one to the other, in the transverse direction. That is particularly true in the as-rolled condition. In fact, tested in the direction of rolling, this silicon-manganese-chrome steel could be easily duplicated by a high manganese. Tested transversely in the as-rolled condition, the benefit of the manganese-silicon-chrome relationship is very distinctly brought out.

F. W. BREMMER.—Unfortunately, it was impossible to obtain a standard Izod specimen from the wall thickness in the standard casing sizes. We were unable to get any impact samples in the as-rolled condition, on account of the wall thickness and because of the curved section, which also cuts down the section which you are able to obtain from a casing. We felt, though, that we covered the matter of impact resistance by flattening these rings and by crushing the cropped ends of each tube. We feel there is no question that this material is ductile and tough, as evidenced by those two tests.

A. B. KINZEL.—At our laboratories material has been available in other shapes, so we could get standard impacts. The order of impact is about the same in the as-rolled as in the normalized state. It lines up with the yield point, reduction in area and elongation, very nicely indeed, and does not show the marked difference one sometimes gets in steels that show the same static physical properties in the as-rolled and normalized state.

E. C. WRIGHT, Pittsburgh, Pa. (written discussion).—Mr. Bremmer is entitled to the highest commendation for the mill practice he presented in this paper. Many years ago, manufacturers of welded boiler tubes found that the flattening test applied to the crops from both ends of every tube made was the best means of insuring maintenance of the standard of quality. The ring-flattening test causes stresses in tension and compression in the material of both the inner and outer surfaces of the tube. From an inspection of the flattened test piece it is possible to judge with accuracy the quality of the material. It has been proved by elaborate investigations that if both crop ends pass this test the probability that the tube is of at least equal quality is extremely large. These characteristics, combined with its application to every tube, make this test of far greater value than any other practicable method. If the flattening is carried to the point of fracture, additional information is obtained. This can be done only at an increased cost, but as it is in the present state of knowledge a complete substitute for the expensive and little understood impact test, it might well be worth the cost when applied to materials with ultimate strength above 90,000 lb. per square inch. At least one manufacturer is using extensively this method of flattening to fracture.

Mr. Bremmer's statement that less than 1 per cent. of the tubes fail to pass a flattening test to 10 times the wall thickness for the distance between plates is confirmed by the experience of other makers. This is striking evidence of the uniformly high quality of tubes made by the Nicholson method for seamless tubes.

Pipe used for oil-well casing, or for rotary drilling, is subjected to stresses of which the magnitude cannot be determined. Our knowledge of them is limited to the information to be obtained from failures of materials of known properties. In this way we have learned that drill pipe may twist off in material having a torsional resistance several times the maximum torque the drive can exert; that increasing the weight of drill pipe is almost useless in preventing failures, and increasing the diameter of the pipe relative to the diameter of the bit is effective. In casing, failures occur under circumstances that make it logically impossible to conceive how the known strength could have been exceeded.

Conditions such as these dictate the use of a material that will have a plastic flow of considerable magnitude before the ultimate strength is reached. This is recognized in the specifications of the American Petroleum Institute by making the permissible elastic ratio as low as 0.6 for the material of higher ultimate strength and less for softer grades.

Containers for gases under high pressures offer another example of the use of materials subject to stresses of more or less unknown intensities. Here reduction in weight is of great importance. Many years' study and investigation have led to abandoning the practice of heat-treating containers by quenching and drawing, with the resulting high elastic ratios and uncertain factors. A gas-container failure is much less disastrous if fragmentation is avoided. That is to say, a high degree of ductility is required. This quality is secured by simply normalizing.

Mr. Bremmer would seem to be in accord with this general line of thought, for while he reports in his paper data on the physical properties of various steels quenched and drawn with high elastic ratios, in his product it would appear from his description of flattening-test results that he uses a steel in the as-rolled state with an elastic ratio under 0.65 for grade D. The physical properties of the analyses proposed for grade E casing, as shown in Table 7, also indicate elastic ratios under 0.65.

C. L. SHIRLEY, Tulsa, Okla. (written discussion).—In the steels mentioned in Table 1 of Mr. Bremmer's paper the percentage of elongation decreases as the tensile strength and yield point increase. Original pipe steel was of the Bessemer type, with a low carbon and high phosphorus content, and the present mill practice follows in a general way the original development necessary to make tubes from this character of steel. Present seamless-tubing mill practice is adapted to use 0.35 to 0.55 carbon steel. If alloy steel is to be used in the rolling of tubes, drastic changes in mill practice must be made. Thermal control was formerly handled by the time element and all mill machinery was arranged to obtain a maximum production by allowing required time between processes. This thermal control was carried on by exposure in still air or such air currents as naturally existed in the mill.

Mr. Bremmer points out in his paper the considerable trouble that steel manufacturers have in trying to make commercial steel and to change their normal processing as little as possible. The selection of a silica-manganese-chrome alloy was no doubt largely determined by the fact that it could be easily adjusted to present mill practices. As expected from mill experience, nickel alloys would be eliminated on account of the difficulty that is encountered when they are worked hot.

The average tests on grade C very nearly meet the requirements on grade D pipe. The mill manufacturer should be complimented for manufacturing such a high-grade tubing from medium-carbon, nonalloy steels; in fact, tubes of this character permitted working at greater depths than is usually recommended under the factor of safety columns in the manufacturers' bulletins. The use of high-grade low-priced steels, such as the silicon-manganese-chrome type, will be an important factor in the economic exploitation of petroleum reserves.

Electrolytic Iron from Sulfide Ores

By Robert D. Pike,* George H. West,† L. V. Steck,† Ross Cummings† and
B. P. Little,† Emeryville, Calif.

The first authentic description of an iron bath for the deposition of iron is probably that of Bottger in 1846, who used a bath containing ferrous sulfate and ammonium chloride. In 1861, Kramer deposited iron from ferrous chloride solution. Electrolytic iron was produced in 1869 by Bietz, who used it for making some magnetic tests. In the same year, Klein is said to have worked out his process.

Jacobi[1] in 1869 described the results obtained in electroplating with iron on copper for making dies and plates for bank notes, by Klein's process. A letter from Klein to Jacobi describes the bath more fully. It consisted of $FeSO_4 + (NH_4)_2SO_4$.

Lenz[2] described some properties of electrolytically precipitated iron. He used Klein's bath, $FeSO_4 + MgSO_4 + MgCO_3$, to neutralize and obtained fine-grained and hard iron. His conclusions were as follows:

1. Electrolytic iron and copper contain gases, notably hydrogen.

2. The volume of gas absorbed by iron varies within wide limits, but it is easy for iron to take up very considerable quantities of gas.

3. The absorption of gas is principally in the first formed layers of iron.

4. When iron is heated, gas begins to come off below 100°, principally hydrogen.

5. Heated to redness, reduced iron oxidizes in water, in part at least at the expense of the oxygen of the water, decomposing it and setting free hydrogen, which is partly or wholly absorbed.

Siemens,[3] in 1889, was the first to propose a general process embodying a step for leaching a sulfide mineral with ferric chloride or sulfate and a step for regenerating the leach and depositing iron on a cathode in a diaphragm cell. So far as is known, Siemens did not carry out his patent

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[1] M. H. Jacobi: *Bull.*, Acad. Imper. des Sci. de St. Petersburg (1869) **13**, 40.
   Brit. Assn. *Rept.* 67 (1869).

[2] R. Lenz: *Jnl. f. prak. Chem.* (1849) **108**, 438.
   Pogg. Ann. (1871) Erg. 5, 242.

[3] W. Siemens: U. S. Patent 415576.

specifications in practice, but his disclosures clearly show the general basic principles followed by all later workers, including the authors, in producing electrolytic iron from sulfide ores.

A thorough study of the gases obtaining in electrodeposited iron was made in 1897 by Winteler,[4] who also was the first to make the observation that hydrogen is deposited unevenly on the deposit and causes strain; he offered the latter as an explanation for the bending of the cathode during deposition, this having been noticed by previous investigators. Haber[5] commented upon Lenz's and Winteler's results. He obtained some specimens of plated iron from the Austrian Mint, where deposition according to Klein's method for the printing of bank notes had been installed. He determined the relation H/Fe for some of his specimens and found results to compare well with those obtained by Lenz.

In 1900, Merck[6] took out a patent for the use of ferrous chloride solutions, in which he recommended high temperatures and agitation of the solution. The solution containing 1:1 $FeCl_2$ and water was heated to around 70° C. and then electrolyzed under a current density of 28 to 37 amp. per sq. ft. (3 to 4 amp. per sq. dm.).

In 1904, the first serious attempt to produce electrolytic iron in quantities was made by C. F. Burgess and C. Hambuechen.[7] After a series of tests conducted over a long period, these authors finally found that the best solution to employ for deposition of iron was a mixture of ferrous and ammonium sulfates. A current density of 6 to 10 amp. per sq. ft. (0.65 to 1.1 amp. per sq. dm.) with an average e.m.f. of 1 volt was used at a temperature of 30° C.

This process has come to be known as the Burgess process, and with some variations has been the basis for most commercial manufacture of electrolytic iron in the United States. A Burgess plant was operated for some years by the Western Electric Co., as described by Speed and Elman.[8] In this variation of the process the anodes were cast steel and the bath was carried slightly on the alkaline side, in order to purposely deposit considerable oxides in the cathode so that the latter would be brittle and easily ground up in a later stage of the process. It was not necessary to make a pure grade of iron. More recently another plant embodying a further modification of the Burgess process was installed by the Westinghouse Electric & Mfg. Co.[9] In this plant the object

[4] F. Winteler: *Ztsch. f. Electrochem.* (1897–98) **4**, 338.

[5] F. Haber: *Ztsch. f. Electrochem.* (1897–98) **4**, 4103.

[6] Merck: Deutsche Reich Patent 126839.

[7] C. F. Burgess and C. Hambuechen: *Trans.* Amer. Electrochem. Soc. (1904) **5**, 201.

[8] B. Speed and G. W. Elman: *Jnl.* Amer. Inst. Elec. Engrs. (1921) **40**, 596.

[9] P. H. Brace: *Jnl.* Amer. Inst. Elec. Engrs. (1925) **44**, 922.

was to produce a pure grade of iron for melting in the manufacture of alloys for electromagnetic machinery and instruments. Commercially pure iron anodes were employed, but even with this precaution, the refining range of the process was very small and often cathodes would be produced undesirably high in either carbon or sulfur or both.

In 1914, Guillet[10] described the so-called Beve or Grenoble process, installed commercially at Grenoble, France. This process employs as a bath a hot neutral solution of ferrous chloride to which iron oxide is added as a depolarizer, with cast iron anodes and rapidly rotating mandrels for cathodes. The product is a tube of electrolytic iron of good purity. A later description of the Grenoble process is by Escard,[11] who gives the following analysis: Fe, 99.967 per cent.; C, 0.008; Mn, 0.009; P, 0.002; Si, 0.014; S, trace.

C. P. Perin was instrumental at a later date in installing a commercial Grenoble plant at Niagara Falls.[12]

During the World War processes were worked out for building up worn machine parts with electrolytic iron. Descriptions of these processes are given by W. A. Macfadyen and B. H. Thomas.[13]

C. F. Burgess and his associates, beginning in 1906, published a long series of articles on the properties of electrolytic iron and its alloys.[14]

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[10] L. Guillet: *Jnl.* Iron and Steel Inst. (1914).
  Electrician (1914) **74**, 79.
  Engineering (1914) **98**, 413.
[11] J. Escard: *Génie Civil* (1919) **75**, 165, 199, 225.
  Elec. Rev. (1920) **76**, 610.
[12] Anon: *Iron Age* (1921) **116**, 675.
[13] W. A. Macfadyen: *Engineering* (1919) **108**, 827.
  B. H. Thomas: *Automotive Ind.* (1920) **43**, 418.
[14] These articles are in part as follows:

  C. F. Burgess and A. H. Taylor: Magnetic Properties of Electrolytic Iron. *Trans.* Amer. Inst. Elec. Engrs. (1906) **25**, 459; *Electrochem. and Met. Ind.* (1906) **4**, 208.

  C. F. Burgess and J. Aston: Physical Properties of Iron-copper Alloys. *Trans.* Amer. Electrochem. Soc. (1909) **16**, 241.

  Certain Alloys for Permanent Magnets. *Ibid.* (1910) **18**, 255.

  Magnetic Properties of Electrolytic Iron and Some Commercial Sheets. *Met. & Chem. Eng.* (1910) **8**, 191.

  Strength of the Alloys of Electrolytic Iron and Monel Metal. *Ibid.* (1910) **8**, 452.

  Electrical and Magnetic Properties of Alloys of Fe-Si. *Ibid.* (1910) **8**, 131.

  Magnetic and Electrical Properties of the Fe-Cu Alloys. *Ibid.* (1910) **8**, 79.

  Magnetic and Electrical Properties of the Fe-Ni Alloys. *Ibid.* (1910) **8**, 23.

  Electrical Resistance of Alloys of Iron. *Trans.* Amer. Electrochem. Soc. (1911) **20**, 205.

  C. F. Burgess and J. J. Crowe: Critical Ranges A_2 and A_3 of Pure Iron. U. S. Bur. Stds. *Sci. Paper* 213 (1914).

Following Burgess, T. D. Yensen[15] took up the intensive study of the relation of pure iron to magnetism and has continued his work without interruption to the present day. Yensen's work proves that even amounts of carbon and sulfur of the order of 0.001 per cent. have a marked effect in increasing the hysteresis loss of iron, and indicates that with entirely pure iron the hysteresis loss would approach zero. More recently he has found that oxygen has a bad effect on the magnetic properties and has shown that a small amount of carbon is valuable for elimination of both carbon and oxygen in vacuum melting.

Brace and Ziegler[16] have made a study of gases given out by electrolytic iron when melted *in vacuo*.

It will be seen from the above that all commercial developments for the manufacture of electrolytic iron have been based upon the use of soluble anodes but that Siemens, as far back as 1889, had proposed a process for making it from sulfide ores in a cell with an insoluble anode.

About 1920, Eustis began his attempts to carry out the Siemens proposal, utilizing pyrrhotite ores from Canada. After an initial investigation at Massachusetts Institute of Technology, a laboratory and pilot plant were installed at Milford, Conn. The most complete available account of the Milford work is that by Belcher.[17] The senior writer visited the Milford plant in November, 1923, just before work was finally discontinued, and is indebted to Belcher and his associates for a full account of their results. It was the original plan at Milford to operate the pilot plant but this plan was abandoned because of difficulties with the iron cells, and no balanced continuous operation between leaching plant and iron cells was ever carried out. However, a great amount of laboratory work was done on leaching pyrrhotite, in treating

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[15] A partial list of publications of T. D. Yensen:

Magnetic and Other Properties of Electrolytic Iron Made in Vacuo. *Bull.* 72, Eng. Expt. Sta. Univ. of Ill. (1914); *Proc.* Amer. Inst. Elec. Engrs. (1915) 34, 237, 2445.

Magnetic and Other Properties of Fe-Si Alloys Melted in Vacuo. *Bull.* 83, Eng. Expt. Sta. Univ. of Ill. (1915).

Effect of Boron upon the Magnetic and Other Properties of Electrolytic Fe Melted in Vacuo. *Bull.* 77, Eng. Expt. Sta. Univ. of Ill. (1915).

Preparation of Pure Alloys for Magnetic Purposes. *Trans.* Amer. Electrochem. Soc. (1917) 32, 165.

Magnetic and Other Properties of Fe-Al Alloys Melted in Vacuo. *Bull.* 95, Eng. Expt. Sta. Univ. of Ill. (1917).

T. D. Yensen: U. S. Patent 1277523 (1918).

Magnetic and Electrical Properties of Ternary Alloys Fe-Si-C. *Jnl.* Amer. Inst. Elec. Engrs. (1924) 43, 558.

On the Road to Pure Iron and Some of Its Indicated Properties. Amer. Electrochem. Soc. (1929). Preprint.

[16] P. H. Brace and N. A. Ziegler: *Proc.* Inst. of Metals Div., A. I. M. E. (1928) 544.

[17] D. Belcher: *Trans.* Amer. Electrochem. Soc. (1924) 45, 455.

pyrite with ferric chloride and in depositing small iron tubes on rotating mandrels in a diaphragm cell. Much attention was also given to the effect of various impurities upon the deposit.

The writers made use of much of the Milford data and experience and are indebted to Mr. Belcher and his associates as well as to Messrs. Eustis and Perin for the opportunity to examine the results.

The work at Milford was followed and to some extent elaborated upon by R. J. Traill and W. R. McCleland.[18] No drawing is given of the cell employed, but judging from the description, it was the virtual duplicate of the small laboratory cell used at Milford, being constructed of ebony asbestos wood, 12 in. long, 12 in. deep and 7¼ in. wide, inside dimensions. The cathode, a cylindrical steel mandrel, is separated from the graphite anode plates by an asbestos cloth diaphragm. The cathode has a deposition surface of approximately one square foot, and is rotated at a speed of 250 to 350 r.p.m. The cell temperature is 80° to 90° C.; current density, 100 amp. per sq. ft. (11 amp. per sq. dm.) and cell voltage 4.0 to 4.4. The best operating conditions were found to be with acidity pH 3.7 to 3.9, an iron content of 170 to 185 g. per liter, absence of ferric in the catholyte and pure electrolyte. Cathodic current efficiency was about 94 per cent. The operation was on a laboratory scale and no thick deposits of iron are recorded. As an example, one run was made for 5 hr., producing a deposit 0.03 in. thick, weighing 518 g. Real difficulties in depositing iron begin only when the deposits are somewhat thicker than this. Difficulty was experienced in stripping the deposit from the mandrel and no successful procedure was evolved. This same difficulty was encountered and not overcome by the Milford workers. Many valuable data are recorded on the specific effect upon the deposits of certain impurities in the electrolyte and means for their removal.

The work was also extended to include treatment of pyrrhotite of low gold and copper content. A further and very interesting extension of the general idea lay in treating ilmenite for making of electrolytic iron and titanium oxide. In the latter process the iron oxide of the ilmenite is reduced to sponge iron before leaching.

PRESENT INVESTIGATION

The writers first undertook the work recorded in this paper in 1923, before the Canadian work, but the publication of the latter in so far as it refers to sulfide ores does not appear to have brought forth essentially new data not earlier available from the Milford experiments. The senior writer's viewpoint at the beginning was predicated upon a desire for treat-

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[18] R. J. Traill and W. R. McCleland: Investigations in Ore Dressing and Metallurgy. *Bull.* 72, Dept. of Mines, Mines Branch, Canada.

ing copper concentrates mostly produced by Engels Copper Mining Co. in California, following in a general way the published accounts of the Milford flow sheet. The main thing was the recovery of copper, the electrolytic iron being viewed as a by-product of secondary importance. It seemed .logical to adapt as a whole the Milford results, but upon investigation it was found that the Milford experiments had not resulted in a balanced and continuous pilot-plant operation, but had been carried out on a strictly laboratory scale; nor had anything approaching thick commercial deposits of iron been made; nor was any indication discovered of the development of an iron cell which could be continuously operated over long periods of time and on a commercial scale.

At the outset of this work, the problems requiring attention were the following:

1. To develop a practical diaphragm cell for production of electrolytic iron from solutions of ferrous chloride, at the same time producing a leach of sufficient strength to decompose pyrrhotite, chalcopyrite or chalcocite.

2. The production of an iron cathode of almost 100 per cent. purity.

3. The maintenance of the electrolyte at a satisfactory standard condition of purity; to determine this condition, and to provide an inexpensive means of making up unavoidable losses of chlorine, as well as to bleed from the electrolyte elements which might accumulate.

(Considerations of advantages of electrodeposition of iron from chloride solutions, including the practical impossibility of depositing a low-sulfur iron from sulfate solution, and the greater activity of ferric chloride as a leach, pointed conclusively to the use of straight chloride electrolytes, and the use of a sulfate electrolyte was never given serious consideration.)

4. To devise a method of leaching that would effect practically complete extraction of copper from copper concentrates, at the same time yielding a high extraction of the iron.

5. To maintain for a considerable period of time, on a semicommercial scale, a complete balanced operation between leaching of a sulfide ore or concentrate and electrodeposition of iron.

The following paper presents a detailed account of the authors' work, looking toward a solution of these problems.

THE FLOW SHEET

The flow sheet as illustrated in Fig. 1 is suitable for handling chalcopyrite concentrates. These are leached in tank $1a$ with boiling hot leach solution containing 10 to 11 per cent. total Fe, of which 4 to 5 per cent. is Fe^{+++}. In order to obtain as high an extraction of copper as possible, the Fe^{+++} is only partly reduced in $1a$. Reduction may be

completed in 1b with pyrrhotite. The tails are filtered in 2, and in 3a, b and c silver is cemented out on copper. The copper is cemented on iron in 4a and 4b, and the settled sludge of cement copper is filtered in 5. Decanted copper-free solution goes through tower 6, where it is treated with H_2S to remove the last traces of copper and any small amount of Zn which may be present. The precipitated sulfides are filtered out in 7, and the solution then passes through disk evaporator 8, where accumulated water is removed. This is made necessary because all heating in the cycle is accomplished by injection of live steam into the
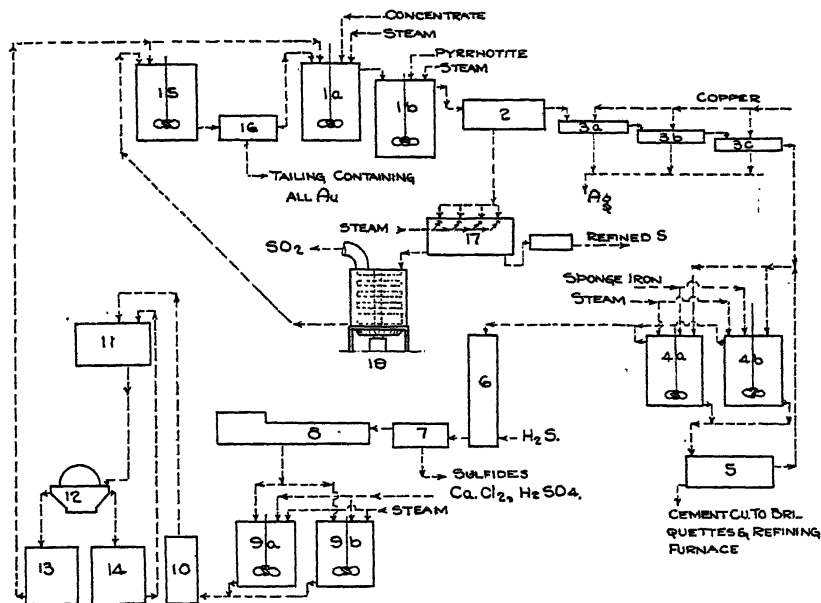
FIG. 1.—FLOW SHEET.

solutions. The solution after evaporation in 8 is a practically pure solution of ferrous chloride, containing 12 per cent. Fe^{++} and only traces of Fe^{+++}. This solution goes to the final correction tanks 9a and 9b, where a small amount of sulfuric acid is added to bring the pH to 2.5. Lost chlorine is restored by the addition of $CaCl_2$. The Ca^{++} is precipitated by SO_4, which is supplied to the cycle by a method to be described. The precipitated $CaSO_4.2H_2O$ forms a voluminous free-filtering precipitate which cleanses the solution of colloidal matter. After filtration in 10, the solution passes to electrolytic storage tank 11, whence it is fed to the electrolytic iron cells, 12. Some of the catholyte from these cells drains into 14 and is circulated back to 11. The anolyte drains back to 13, whence it returns to the leaching steps of the cycle.

Taking, for example, a chalcopyrite concentrate such as those obtained from the Walker mine in California, the extraction of copper in the leaching tanks 1a and 1b will be 90.8 per cent.; of silver, 83.9 per cent. and of iron, 83.3 per cent. The tails contain 49 per cent. of free sulfur, corresponding to 73 per cent. of the total sulfur in the concentrates, (for analyses see Table 1). These tails are next treated by any suitable method for recovery of their sulfur in 17 and are then roasted in 18. The roasting is so controlled as to make enough sulfate to be equivalent to the CaCl₂ added in the tanks 9a and 9b. The roasted tails go to tank 15, where they are leached with a portion of the return leach from the cells. As stated later, this second leaching can be accomplished equally well by use of a portion of the completely reduced solution from 1b, because copper oxide is soluble in ferrous chloride. The final tails, which are removed in filter 16, contain about 0.3 per cent. Cu and all of the original Au. The latter will have been concentrated as compared to the original concentrates in the ratio of 4 to 5: 1.

Much the same results are obtained with Engels concentrates (Table 1), which are mostly bornite with some chalcopyrite but have a considerably larger amount of insoluble matter and less iron and sulfur than the Walker concentrates.

If the copper-bearing pyrrhotite is used exclusively as the raw material, the flow sheet is simplified. Only one leach tank is employed and the extraction of copper is so high that treatment for additional recovery is not justified. The tails from this first leach will contain a considerable amount of free sulfur. As an example of the use of pyrrhotite Anyox pyrrhotite was tested in the pilot plant. The extraction of iron was 88.9 per cent.; of copper, 81.8 per cent. The tails contained 49 per cent. of free sulfur, corresponding to 76.5 per cent. of the total sulfur in the heads.

The Pilot Plant

The pilot plant was operated almost continuously from Sept. 25, 1925 to Jan. 31, 1926, during which time 49 leaching cycles were completed, using the same electrolyte. In eight of these, sponge iron or scrap iron was used to reduce the ferric iron of the cell solution; in one, Anyox pyrrhotite alone; in five, Walker concentrates and pyrrhotite; and in the remaining 35, Engels concentrates and pyrrhotite. The Walker concentrates were dried and ground to 96 per cent. − 200 mesh. One charge of Engels concentrates was ground to 99 per cent. − 200 mesh, the remainder was charged as received.

The first complete metallurgical balance was made two months after the first leaching operation, and thereafter complete metallurgical balances of the entire pilot plant operation were made every week or 10 days.

During the entire period, there was continuous improvement in control of plant losses, in mechanical design and operation of the electrolytic cell, and in stripping practice.

The conditions of cell operation were varied many times; for example, iron was deposited under different conditions of cathodic current density, electrolyte temperature, anolyte circulation, rotational speed of cathode and anode construction. In the same manner, variations were made in leaching practice and electrolyte purification, all with a view to assembling the details that would make the process the most economic consistent with efficiency. The total amounts used were: Engels concentrates, 10,103 lb.; Walker concentrates, 835 lb. and pyrrhotite 1997 lb. A summary of the analyses of these materials is shown in Table 1.

TABLE 1.—*Summary of Analyses of Engels and Walker Concentrates and Pyrrhotite Used in the Operation of Pilot Plant*

August 20, 1925–January 31, 1926

	Engels Concentrates, Per Cent.	Walker Concentrates, Per Cent.	Anyox Pyrrhotite, Per Cent.
Cu.................................	27.18	23.65	2.65
Fe (Acid-soluble)..............	15.04	28.8	46.6
S.................................	17.01	29.25	29.0
Insoluble.......................	30.00	10.16	6.5
SiO$_2$..........................	19.47	7.34	0.53
Total Fe.......................	16.81	30.9	47.25
Ca...............................	1.76	0.14	4.28
Mg...............................	2.27	0.31	0.42
Al...............................	3.56	0.92	1.38
Au, oz. per ton................	0.04	0.20	Tr.
Ag, oz. per ton................	6.26	6.10	0.30
Zn...............................	0.33	0.40	1.25
Na...............................	0.13	0.25	0.07
K................................	0.86	0.16	0.36
Mn...............................	0.41	0.18	0.21
As...............................	0.21	0.02	0.04

Screen Analysis

−200	77.6
−150 + 200	10.9
−100 + 150	8.5
+ 100	2.8

The principal secondary raw material used in this process is the iron for cementing the copper. The authors used mostly, for this purpose, a pure grade of detinned scrap in loose bales. This scrap is a pure form of mild steel with, perhaps, small amounts of tin remaining with the

steel. A considerable amount of sponge iron was also used for this purpose (Table 2).

TABLE 2.—*Analysis of Sponge Iron*

	No. 2134, Per Cent.	No. 3263, Per Cent.
Fe...............................	85.1	70.0
FeO..............................	0.5	
Fe$_2$O$_3$...........................	1.0	
Total soluble Fe.....................	86.6	
SiO$_2$..............................	6.23	5.65
Total fusion Fe.....................		77.2
Ca...............................	0.107	0.07
Mg..............................	0.428	0.719
Al...............................	0.998	1.014
Carbon...........................	0.353	

In carrying out the full-scale operation of the pilot plant, only the so-called No. 1 chloride leach was used, corresponding to the operation in tanks 1a and 1b, Fig. 1. The tails from 2 were allowed to accumulate and the operations corresponding to removal of sulfur, 17, roasting, 18 and second leaching, 15 were all carried out on a smaller scale. The separate cementation of silver was also tried on a smaller scale, but with these exceptions the pilot-plant operation included in its full cycle all of the steps shown in Fig. 1, and the electrolytic cell was at all times balanced against the leach.

ELECTROLYTIC IRON

In all, 2923 lb. of electrolytic iron were produced. The average analysis was as follows: C, 0.005 per cent.; S, 0.007; Cu, 0.006. P, Si, Mn, Ni, Co, Cd, As, Zn, Sn and Pb absent. In several samples, the sulfur was as low as 0.003 and copper, 0.004, and we believe that these limits could be held in regular operation. The cathodes were about 0.2 in. thick and were of homogeneous iron entirely free from porosity. The following experiment illustrates the remarkable properties of this iron. The somewhat rough surface of deposition of an annealed cathode was machined, giving a plate 0.2 in. thick. This plate was rolled cold to 0.109 in. and this cold-rolled plate, without annealing, was stamped cold into the telephone relays (Fig. 2). No failures resulted and the conclusion was that the iron showed very little work hardening, and in that respect was different from all available iron. It was also considerably softer magnetically than available grades of commercially pure iron. It was noticed that the 0.109-in. plate could be cold-rolled down to a 30-gage strip without annealing and that the resulting strip was soft

and very flexible. Fig. 3 shows a strip cold-rolled from the original annealed cathode without annealing between passes. Most of the iron was used for the experimental production of special electromagnetic sheets by alloying with other elements, in the laboratories of Westinghouse Electric & Mfg. Co. at East Pittsburgh.

Photomicrographs are shown in Figs. 4, 5 and 6 and a 48-in. cathode in Fig. 7. Figs. 5 and 6 are etched deeply with ferric chloride. The latter is of a commercially pure iron that develops a sort of "etching pit" absent in the electrolytic iron, which shows a perfectly uniform etched surface except for slightly different attacks of the reagent on grains of different orientation.
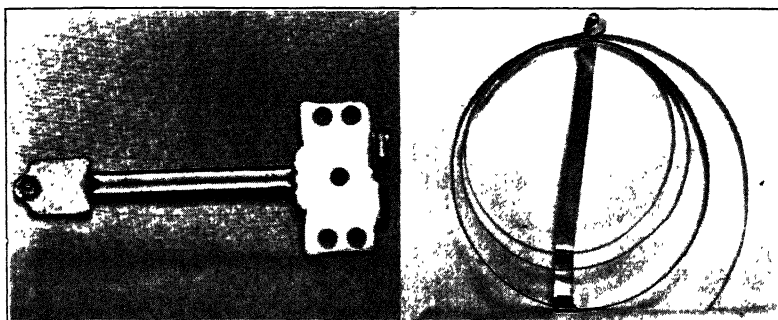
FIG. 2.—TELEPHONE RELAY STAMPED   FIG. 3.—COLD-ROLLED STRIP FROM
FROM COLD-ROLLED PLATE.   ORIGINAL ANNEALED CATHODE.

The authors have not made a complete survey of the physical properties of this pure iron, but have made a few observations, which with those of others, bringing out as they do some sharp differences from ordinary pure irons, seem worth while recording. Observed properties are given in Table 3.

TABLE 3.—*Properties of Electrolytic Iron*

	ELECTROLYTIC IRON	COMMERCIALLY PURE O. H. IRON
Annealed at 1000° C. and cooled slowly in furnace, Brinell hardness number.......	47	73
Heated at 1000° C. and quenched in water, Brinell, hardness number..............	57	110
Ultimate tensile strength, 0.109-in. cold-rolled strip before annealing, lb. per sq. in.................................	66,350	
Same after annealing.....................................	35,300	
Elongation in 2 in. parallel to grain of rolling, per cent........	14	
Maximum permeability of cathode after ordinary annealing....	4,330	
Same after special annealing............................	7,575	
Coercive force after ordinary annealing....................	1.31	
Same after special annealing.............................	0.62	
β at $H = 35$ gilberts per centimeter before annealing..........	16,750	
Same after annealing......................................	16,875	
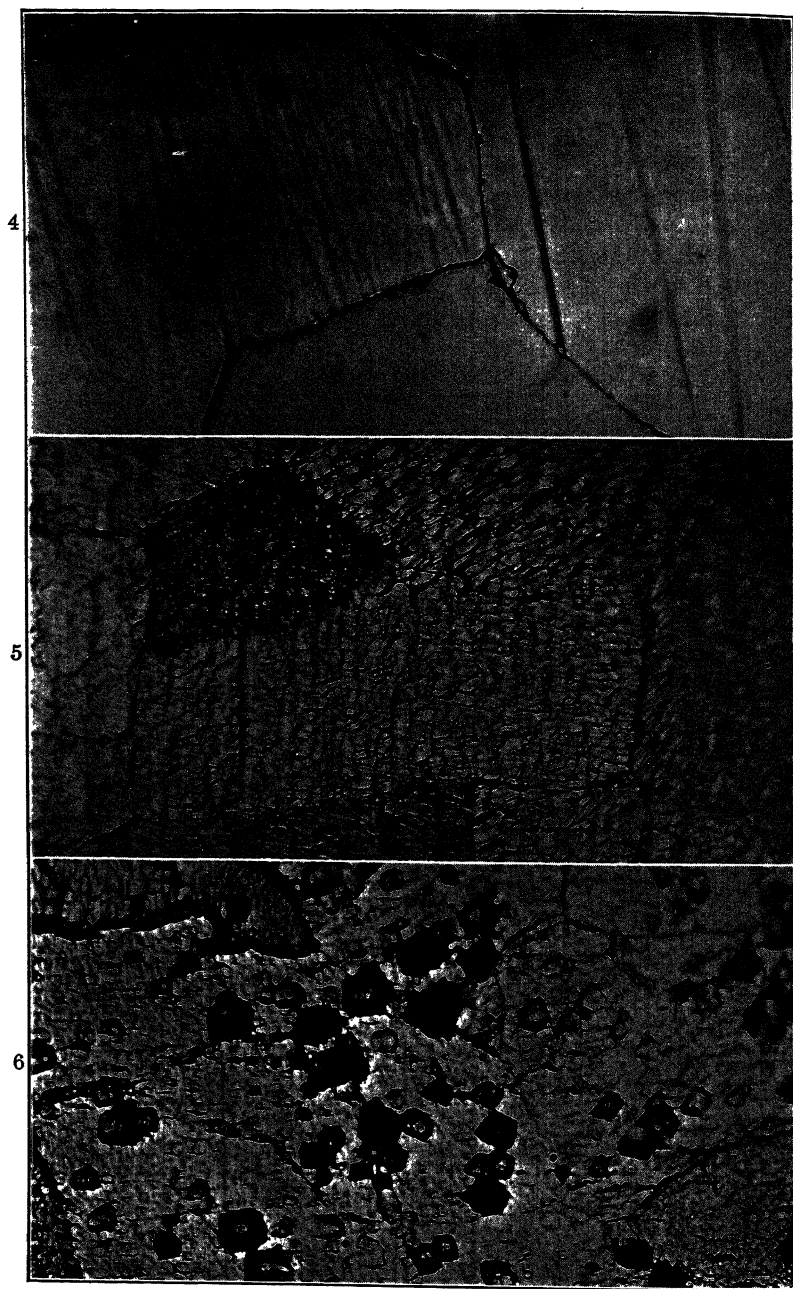
FIG. 4.—ELECTROLYTIC IRON.   HEATED TO 1700° F. FOR 1 HR. AND QUENCHED.
×1000.   Etched 10 sec. with 10 per cent. nitric acid in alcohol.
   FIG. 5.—ELECTROLYTIC IRON.   ANNEALED 1 HR. AT 1800° F. AND QUENCHED.
×1000.
   FIG. 6.—ROLLED ARMCO IRON.   ANNEALED 1 HR. AT 1800° F.   ×300.
          Figs. 5 and 6 etched 1 hr. with concentrated ferric chloride.

According to engineers of Western Electric Co.,[19] who furnished the test data, except on the Brinell hardness, which was determined by the authors, there is not much difference at saturation between the pure electrolytic iron and ordinary magnet iron, but the permeability at low flux densities is much greater with the former. The coercive force for the electrolytic iron is much lower than for ordinary iron.

The difference analytically between commercially pure iron and the iron cathodes used by the authors is not very great, yet the physical differences are considerable. This suggests the chief difficulty in the way of utilizing electrolytic iron in such a way as to take advantage of its
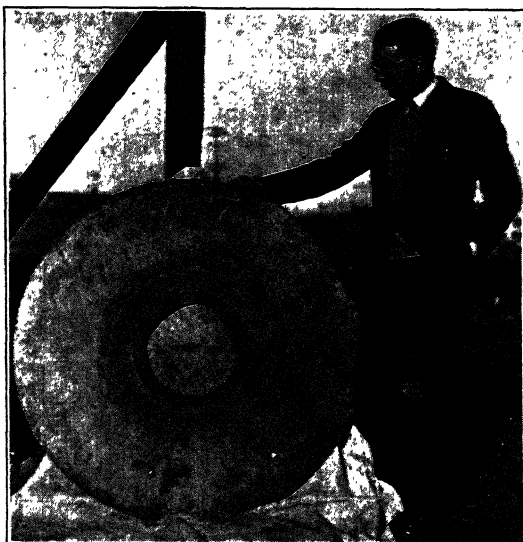
FIG. 7.—48-IN. DISK CATHODE.

properties; namely, that in melting it is almost impossible to avoid taking up minute amounts of impurities which cause a serious impairment of its properties. The writer has proposed a method of producing large commercial masses of pure homogeneous electrolytic iron[20] by welding cathodes together. Heating could be done by induction in an atmosphere of hydrogen and pressure could be employed to weld the cathode together. Thus would be formed a sort of synthetic wrought iron which would be just as pure as the original cathodes. If sheets of this iron, stamped into proper form, could then be impregnated with silicon by cementation,[21] a way would possibly be opened up for taking full commercial advantage of the laws discovered by Yensen.

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[19] Private communication.
[20] U. S. Patent 1675867.
[21] M. A. Sanfourche: *Compt. rend.* (1926) **183**, 791.
  W. Siemens and A. G. Halske: Brit. Patent 245753 (1927).
  L. Guillet: *Compt. rend.* (1926) **182**, 1588.

In present-day methods, silicon-iron sheets are made by rolling from large billets of silicon-iron alloy. This alloy is by no means as easy to roll as pure iron, or even mild steel. When the sheets are punched, about half of the completed silicon-iron sheet is discarded in the punchings and these have little value as scrap for remelting. In the suggested method, the punchings would be pure iron possessing a high value as scrap.

LEACHING

Small-scale leaching experiments were begun in May, 1923, and were prosecuted continuously for one year preceding the operation of the pilot plant. Most of the leaches, which were carried out at atmospheric temperature, were made in 10-gal. earthenware crocks furnished with mechanical agitators. The quantity of ore or concentrate used varied usually over the range of 500 to 2000 g. Heating was accomplished either by injecting live steam or by use of a Pyrex glass coil. Leachings under steam pressure were carried out in a small rubber-lined autoclave. The leach solutions contained 10 to 15 per cent. total iron, of which varying amounts were ferric. In most of this work the material was raw sulfide minerals; namely, chalcopyrite, pyrite, bornite and pyrrhotite. In almost all cases the leach liquor was ferric chloride, and in a few cases, ferric sulfate. The variables investigated as affecting extraction were temperature, time, fineness of grinding, concentration of ferric iron in the leach, and countercurrent as compared with single-stage leaching.

In investigating the effect of temperature, leaches were carried out in rubber-lined autoclaves at gage pressures up to 80 lb. per sq. in., and in connection with this phase of the work we discovered a reversal of the reaction at higher temperatures, which caused the copper to be precipitated at the expense of the iron in the remaining sulfides. No commercial application of this reaction has been suggested, but we investigated it rather completely and it seems worth mentioning because of its possible scientific interest. The principal results are summarized in Table 4. If a pure form of pyrrhotite had been used the enriched precipitant would be expected to contain upwards of 50 per cent. of copper. The precipitated copper mineral is probably covelite. These results are entirely at variance with those of Croasdale,[22] who precipitated copper from sulfate solution on iron sulfides. He determined the maximum possible copper concentration of the enriched precipitant as 17.7 per cent. All of his work was done at atmospheric pressure from sulfate solutions, and it would be interesting to extend our work at higher pressures to sulfate solutions and other iron sulfides.

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[22] S. Croasdale: *Eng. & Min. Jnl.* (1914) **97**, 745.

TABLE 4.—*Precipitation of Copper on Iron Sulfides*

1	2	3	4	5	6	7	8	9	10	11
Run	Time, Minutes	Temperature, °C.	Pressure, Pounds Gage	Precipitant	Weight of Precipitant, Grams	Iron in Precipitant, Per Cent.	Copper in Precipitant, Per Cent.	Weight of Enriched Precipitant, Grams	Iron in Enriched Precipitant, Per Cent.	Copper in Enriched Precipitant, Per Cent.
67	30	170	80	Pyrrhotite	350	46.4	1.3	268	19.4	25.9
68	30	160	60	Pyrrhotite	300	46.4	1.3	219	12.3	29.7
74	30	160	60	Pyrrhotite	270	46.4	1.3	180	9.0	32.6
80	30	160	60	Pyrrhotite	150	46.6	1.35	155	21.8	39.4
77	30	160	60	Iron matte	250	64.0	0.55	182	21.0	34.4
81	60	160	60	Iron matte	200	64.4	0.55	153	19.8	39.5

12	13	14	15	16	17	18	19	20	21
Mesh of Precipitant, Per Cent. through 200	Weight of Original Liquor, Grams	Fe^{+++} in Original Liquor, Per Cent.	Total Iron in Original Liquor, Per Cent.	Copper in Original Liquor, Per Cent.	Weight of Final Liquor, Grams	Fe^{+++} in Final Liquor, Per Cent.	Total Iron in Final Liquor, Per Cent.	Copper in Original Liquor Precipitated, Per Cent.	Iron Actually Used to Precipitate 1 Lb. Cu, Per Cent.
74.4	3630	5.27	13.40	2.03	5695	0.009	10.47	87.9	0.230
74.4	3630	5.27	13.40	2.03	5710	0.12	10.47	82.9	0.327[a]
74.4	3630	5.27	13.40	2.03	5500	0.19	10.80	74.8	0.321
100	3540	none	14.25	2.32	5595	0.02	9.86	71.9	0.611
82	3630	5.27	13.40	2.03	5150	0.10	11.18	83.0	0.465
82	3630	4.40	11.94	2.11	6160	0.03	8.62	80.5	0.314

[a] Example of calculation: 112.3 g. iron went into solution; 191.5 g. Fe^{+++} in original liquor, 6.90 g. Fe^{+++} in final liquor. Fe^{+++} reduced, 184.6 g., requiring solution of 92.3 g. iron. Iron used for precipitating copper, 112.3 − 92.3 = 20.0 g. This precipitated 61.1 g. copper. Ratio 20.0/61.1 = 0.327.

The general conclusions from the small-scale leaching experiments were that 85 to 90 per cent. of the copper could be extracted from chalcopyrite concentrates in from 2 to 3 hr.   The general conditions for successful leaching are:

1. Concentration of total iron, 10 per cent. or over;
2. Concentration Fe^{+++} at least 4 per cent.;
3. Boiling temperature;
4. Fine grinding and efficient agitation.

Some experiments were tried in leaching a pyrite containing 4.7 per cent. copper.   The extraction of copper was 90.1 per cent. and of iron, 24.2 per cent.

Countercurrent leaching experiments were tried at moderate temperatures and with low concentrations of Fe^{+++}.   The results are shown in Table 5.   Under these conditions the residue gained iron at the expense of the leach, which is to be contrasted with a high extraction of iron by hot leaches containing higher concentrations of Fe^{+++}.   The comparison is clearly brought out by the records of the leaches on a larger scale in the pilot plant.

TABLE 5.—*Leaches of Moderate Temperature and with Low Concentration of Ferric Iron as Chloride*

Run	Concentrate	Fe^{+++} in Original Liquor, Per Cent.	Fe^{+++} in Final Liquor, Per Cent.	Extraction of Copper, Per Cent.	Extraction of Iron[a]	Total Extraction
124	Engels	1.56	0.60	49.5	48.8	18.2
125	Walker	1.39	0.48	50.1	88.9	11.0

[a] Not extraction but precipitation.

Table 6 brings out a comparison under similar conditions, in the small-scale leach, of the leaching activity of ferric chloride and ferric sulfate.

TABLE 6.—*Comparison of Ferric Chloride and Ferric Sulfate*

Run	Concentrate	Leach	Extraction of Copper, Per Cent.	Extraction of Iron, Per Cent.	Total Extraction, Per Cent.
173	Engels	Ferric sulfate	63.7	21.4	27.7
174	Walker	Ferric sulfate	50.3	41.0	30.7
41	Engels	Ferric chloride	92.3	53.0	38.6
45	Walker	Ferric chloride	85.3	74.4	50.6

LEACHING IN THE PILOT PLANT

The leaching tank was made of wooden staves lined with acid-proof brick.   The diameter inside the brick was 4 ft. 3 in. and the depth 5 ft.

8 in.; capacity, 83 cu. ft. The tank was provided with a rubber-covered propeller 18 in. dia., operating at 130 r.p.m. Boiling temperature was maintained in the contents of the tank during leaching by the injection of live steam. After leaching, the contents were removed by a suction rubber hose, to a centrifugal pump which discharged into a maplewood plate and frame filter press. The tank was first filled with the anolyte liquor from the iron cell. This was brought to boiling point and the con-centrates were added gradually. When it became apparent that no further reduction of the Fe^{+++} would be effected by the con-centrates, the reduction was completed by the addition of pyrrhotite.

Charge 24 is typical with Engels concentrates. The reduc-tion curve for this charge is shown in Fig. 8; P indicates the addition of pyrrhotite. The Fe^{+++} con-tent of the completely reduced leach is about 0.17 per cent. In figuring the charge, the amount of Fe^{+++} in the head liquor is first determined and enough concentrates added to reduce the Fe^{+++} to about 1.2 per cent. In a typical case, this would require 326 lb. of Engels concentrates. In the same typical case, the pyrrhotite required to complete reduction would be 53 pounds.
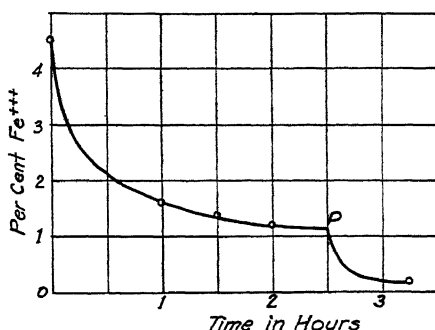
FIG. 8.—REDUCTION CURVE FOR CHARGE 24.

TABLE 7.—*Metallurgical Results in Leaching Raw Concentrates and Pyrrhotite with Boiling Solutions of Ferric Chloride.*

Total Fe in Leach, 10 to 12 Per Cent.; Fe^{+++}, 4 to 5 Per Cent.

	Engels Con-centrates and Anyox Pyrrhotite	Walker Con-centrates and Anyox Pyrrhotite	Anyox Pyrrhotite
Extraction of copper, per cent. of heads....	84.3	90.8	81.8
Extraction of iron, per cent. of heads......	61.2	83.3	88.9
Free sulfur produced, per cent. of heads...	61.8	73.0	76.5
Extraction of silver, oz. per ton..........	85.0	83.9	
Pyrrhotite per 100 lb. of concentrates, lb...	29.8	29.8	
Sulfur oxidized to SO_4, per cent. of heads..	3.82	3.9	11.1[a]

[a] This represents only one leach, while others are averages of consistent results from many leaches. The accuracy of this figure is questionable.

A reduction curve for chalcopyrite (Walker) concentrates is shown in Fig. 9. The average extractions obtained in the original (No. 1)

leach of the raw concentrates and pyrrhotite in the entire pilot plant run, together with other data, are given in Table 7.
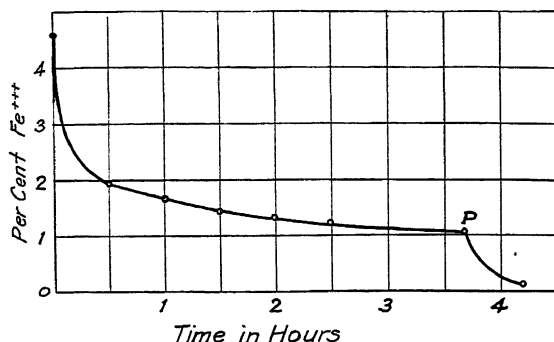
FIG. 9.—REDUCTION CURVE FOR WALKER CONCENTRATES.

SECOND LEACHING

As shown in Fig. 1, the tails from the No. 1 leach are roasted and again leached with anolyte liquor from the cell. This process was not carried out on the full pilot-plant scale, but small quantities of the tails from the No. 1 leach were roasted in a Hoskins muffle furnace and then leached with the anolyte liquor. In these leaches, about one half the total anolyte liquor will be employed and the copper content of the final tails reduced to 0.2 to 0.3 per cent., corresponding to an over-all extraction of over 99 per cent. of the copper. Copper oxide is soluble in ferrous chloride, as well as in ferric chloride,[23] from which it may be concluded that the completely reduced liquor from the No. 1 leach could be used for leaching the roasted tails instead of the anolyte liquor from the cell, and this procedure would have the advantage of removing the necessity for filtering strong solutions of ferric chloride, which presents some engineering difficulties.

CEMENTATION OF THE COPPER

In the pilot plant, no attempt was made to separate the steps for precipitation of silver, copper and zinc; all of these steps were carried out together in one tank, which was of wood and provided with a wooden propeller. Rubber-covered iron racks were placed in the bottom of the tank and the detinned iron scrap was placed on these racks about 18 in. above the bottom and 12 in. from the sides. The propeller caused the solution to circulate freely through the iron and the copper went to the bottom of the tank, whence it was flushed out occasionally. In carrying

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[23] W. E. Greenawalt: Hydrometallurgy of Copper, 352. New York, 1912. McGraw-Hill Book Co.

out an operation, the copper-bearing liquor was run in and brought to 90° C. and a small amount of sulfuric acid was added (6.4 c.c. H_2SO_4, sp. gr. 1.84, per 100 lb. of solution). A qualitative test for copper was run at half-hourly intervals until a negative result was attained; 5 lb. of sponge iron was then added, the steam was turned off and the tank contents gently gassed with H_2S for 2 hr. After gassing, a quantitative test for copper was run on 15 g. of the solution by the method using hyposulfite precipitation and iodide titration. If the iodide titration ran over 1 drop solution = 0.005 g. copper per c.c., the tank was heated again, more sponge iron added, and gassing repeated. Usually the first operation would be sufficient, and that an almost complete removal of copper was effected is proved by the fact that the electrolytic iron contained only about 0.004 per cent., which is remarkable when one considers that about 40 lb. of electrolyte passes through the iron cell for the production of 1 lb. of iron. Thus, we would be justified in concluding that the copper content of the solution is of the order of 0.0001 per cent. The amount of iron required to precipitate copper is shown in Table 8. These figures show that the copper exists in the solution almost entirely in the cuprous condition.

TABLE 8.—*Iron Required for Cementing Copper, Average Results for Pilot Plant Run*

Heads	Iron Required to Precipitate 1 Lb. Copper, Lb.
Engels concentrates	0.582
Walker concentrates	0.597
Anyox pyrrhotite	0.526
Average	0.568

ACCUMULATION OF IMPURITIES IN ELECTROLYTE

Table 1 shows the presence of calcium, magnesium, aluminum, sodium, potassium, manganese, arsenic and zinc, and it is of great importance to note the accumulation of these impurities in the electrolyte. In connection with the striking of the numerous complete metallurgical balances, the extractions of silicon, calcium, magnesium and aluminum in the leach

TABLE 9.—*Extractions of Si, Ca, Mg, Al*

Element	Extraction, Per Cent.
Si	11.4
Ca	72.2
Mg	60.1
Al	24.3

were noted, as well as their migration throughout the various steps of the process.. The average extraction of these elements in the pilot-plant leach is shown in Table 9.
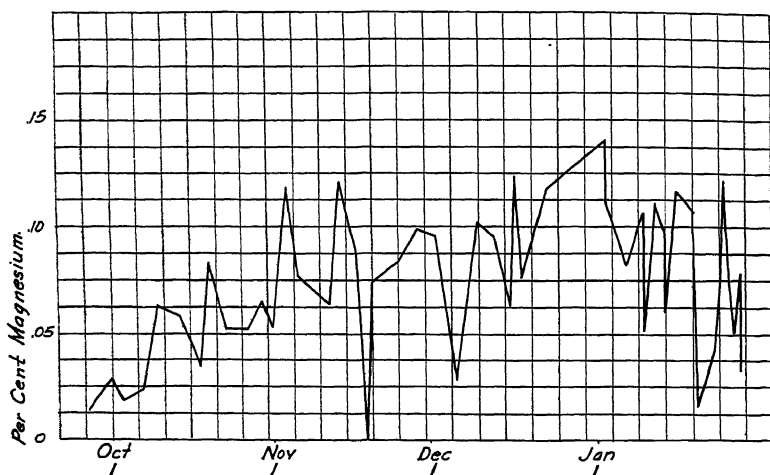
Impurities in Solutions
to Cell Circuit

FIG. 10.—MAGNESIUM IN SOLUTION.
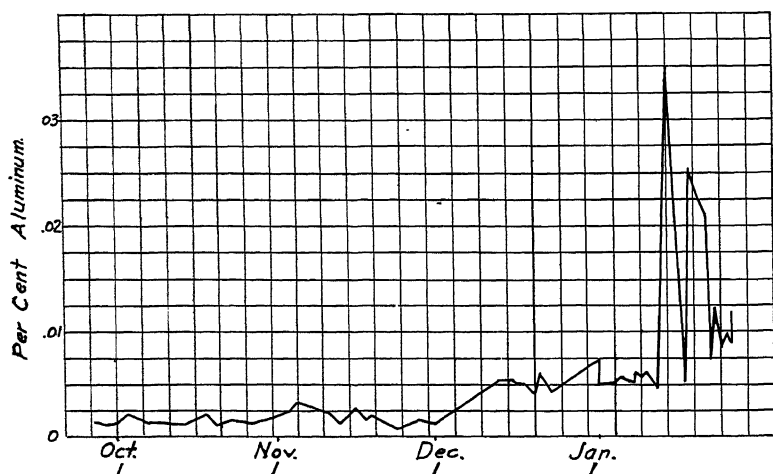
Impurities in Solutions
to Cell Circuit

FIG. 11.—ALUMINUM IN SOLUTION.

The electrolyte was analyzed for these elements, except silicon, after being fully purified and ready for the electrolytic iron cell. The results of these analyses are shown in Figs. 10, 11 and 12. The amount of

calcium is governed by the solubility of gypsum. The per cent. of sulfate in the electrolyte is shown in Fig. 13. In spite of the considerable amounts of magnesium and aluminum that are being continually taken into solution, these elements did not show any noteworthy accumulation.
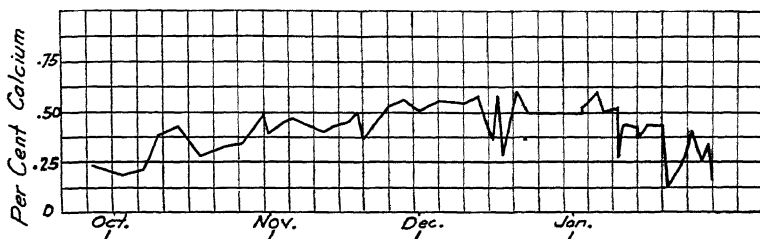
Impurities in Solutions
to Cell Circuit
FIG. 12.—CALCIUM IN SOLUTION.

This was explained by a systematic investigation of the filter-press solids, which were also examined for sodium and potassium. It was found that all of the elements mentioned occurred in the press solids in sufficient quantities to explain their lack of accumulation in the
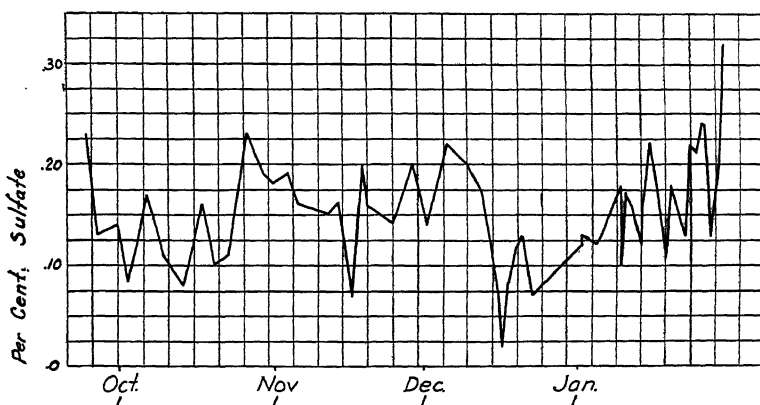
Impurities in Solutions
to Cell Circuit
FIG. 13.—SULFATE IN ELECTROLYTE.

electrolyte. All of these data were finally reduced to balances for each period. Typical balances are shown in Tables 10 and 11.

Covering, as they do, 49 complete leaching cycles, these results may be considered conclusive proof of the fact that the principal soluble and highly electropositive elements, which one would expect to accumulate,

TABLE 10.—*Potassium Balance*

Dec. 5, 1925–Jan. 6, 1926

	Debit, Pounds	Credit, Pounds
On hand in plant solutions 12/5/25...................	7.6	
Into leach tank:		
2324 lb. Engels conc. at 0.97 per cent................	22.5	
492 lb. pyrrhotite at 0.40 per cent.................	2.0	
Tails, press No. 1, 1615 lb. at 0.72 per cent.............		11.6
Tails, press No. 2......................................		none
Tails, press No. 3, 59 lb. at 0.33 per cent..............		0.2
Tails, press No. 4, 190 lb. at 0.19 per cent.............		0.36
On hand in plant solutions 1/6/26.....................		8.7
In lost solutions......................................		2.88
In cell circuit solids..................................		not determined
In evaporator solids..................................		0.8
Unaccounted loss.....................................		7.6
Total..	32.1	32.1

TABLE 11.—*Aluminum Balance*

Dec. 5, 1925–Jan. 6, 1926

	Debit, Pounds	Credit, Pounds
On hand in plant solutions 12/5/25...................	0.5	
Into leach tank:		
253 lb. Engels P-11 at 4.07 per cent................	10.3	
1535 lb. Engels P-12 at 3.36 per cent................	51.6	
536 lb. Engels P-14 at 4.13 per cent................	22.2	
492 lb. pyrrhotite at 0.62 per cent.................	3.1	
227 lb. sponge iron at 1.00 per cent................	2.3	
138 lb. Sil-O-Cel at 0.40 per cent.................	0.6	
Tails, press No. 1.....................................		77.3
Tails, press No. 2.....................................		none
Tails, press No. 3.....................................		0.8
Tails, press No. 4.....................................		0.2
Evaporator solids.....................................		3.5
Cell circuit solids....................................		not determinable
In lost solutions......................................		0.2
On hand in plant solutions 1/6/26.....................		0.5
Unaccounted loss.....................................		8.1
	90.6	90.6

do, as a matter of fact, precipitate in some unknown form. It would be going too far to say that bleeding would never be necessary, but it can be said with confidence that if any is required it will be very small.

It is also a fact that the authors gathered a rather strong impression that the electrolyte "improved" with age in respect to its facility for making good sound deposits of iron.

TABLE 12.—*Zinc, Manganese, Arsenic and Other Elements*

Zn^{++} and Mn^{++} in Filtrate from Press No. 4

Date	Zn^{++}, Per Cent.	Mn^{++}, Per Cent.
11/27/25	0.08	0.101
1/9/26	0.11	0.115
1/31/26	none	0.41

The reduction in Zn^{++} noted between January 9 and January 31 probably results from the fact that shortly after the first of the year the time of the H_2S treatment was increased from 1 hr. to 2 hr. The pick up of Mn^{++} during the same period may or may not have significance, but led to some small-scale experiments on precipitation of Mn^{++} from the plant solutions. These seemed important because of the high manganese extraction in the No. 1 chloride leach, as shown in Table 13.

TABLE 13.—*Manganese Extraction in No. 1 Chloride Leach*

	Engels	Walker	Pyrrhotite
	Run 52	Run 45	Run 50
Mn in heads, per cent....................	0.41	0.18	0.21
Mn in tails, per cent....................	0.40	0.11	0.15
Mn extraction, per cent..................	42	71.6	71.4

The small-scale experiments, which need not be described here, showed that manganese above 1.00 per cent. could be precipitated with H_2S at the expense of some iron. No trace of manganese was ever found in the electrolytic iron.

On January 31, at the end of the pilot-plant run, the electrolyte was examined for cadmium, antimony, arsenic, nickel, cobalt, chromium, lead, tin, and only arsenic was found, to the extent of 0.00006 per cent.

The absence of tin is noteworthy because no doubt small amounts were introduced with the detinned scrap and some tin was discovered in the cell circuit solids. This is explained by the precipitation of some basic salt of tin. In spite of the presence of small amounts of zinc in the solution, none ever appeared in the electrolytic iron.

COLLOIDAL PARTICLES IN ELECTROLYTE

An examination of the electrolyte with the ultramicroscope after the first filtration after the leach showed numerous colloidal particles exhibiting Brownian movement. These became gradually less in number until, after the final gypsum filtration before the electrolytic iron cell, the electrolyte was practically free from colloids. No positive evidence of the fact has thus far been discovered, but it is believed that iron, which is very low in impurities, can be deposited only from electrolytes that are free from colloids. It is known that the addition of organic agents to the electrolyte does contaminate the iron with carbon. It is thought, therefore, that the gypsum precipitate made in the electrolyte just before the iron cell, cleansing the electrolyte as it does of the last trace of colloidal matter, is an important factor in assuring the production of iron of exceptional purity.

THE ELECTROLYTIC IRON CELL

In the first attempt to build a diaphragm electrolytic iron cell the authors followed designs furnished by the Milford workers associated with Eustis and Perin. This cell had fully submerged stationary electrodes. The anodes were of graphite and were enclosed in asbestos bags. This cell was a complete failure because of snags which grew out from the deposit and pierced the asbestos diaphragms. Invariably when a cathode was lifted the opposing diaphragm was torn and the entire cell put out of commission.

Cells of the type employed by Hoepfner[24] seemed to offer a chance for removing this trouble and the problem was eventually solved by use of diaphragm cells with rotating, partly submerged disk cathodes. The cell of this type that was developed in the operation of the pilot plant operated continuously and no diaphragms were injured. Much experimenting was done with rubbing the deposit. At first rubber was used for this purpose but the iron became contaminated with carbon and sulfur. Rubbers of soft iron were finally developed, which operated on the surface of the exposed disks just before they entered the electrolyte. These rubbers seemed to make the deposit more dense and uniform if applied during the first day or so of deposition, but after that they became worn out and were of no further use. The authors do not consider the use of the rubbers necessary during any period of deposition; they may increase the practical period of deposition by a day or so, but this advantage would hardly be expected to compensate for their cost.

The electrolytic iron cell used in the pilot plant is shown in Fig. 14, without its cover. The latter (Fig. 15), which completely covers the exposed part of the disks to keep them from being chilled, is made of cork

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board assembled on a steel frame. The diaphragm (Fig. 16) is made of pure woven asbestos cloth vulcanized on to a rubber-covered steel frame. This slips into a groove in the cement body of the cell and is cemented into place by portland cement mortar. The anode, made up of graphite plates, is illustrated in Fig. 17.
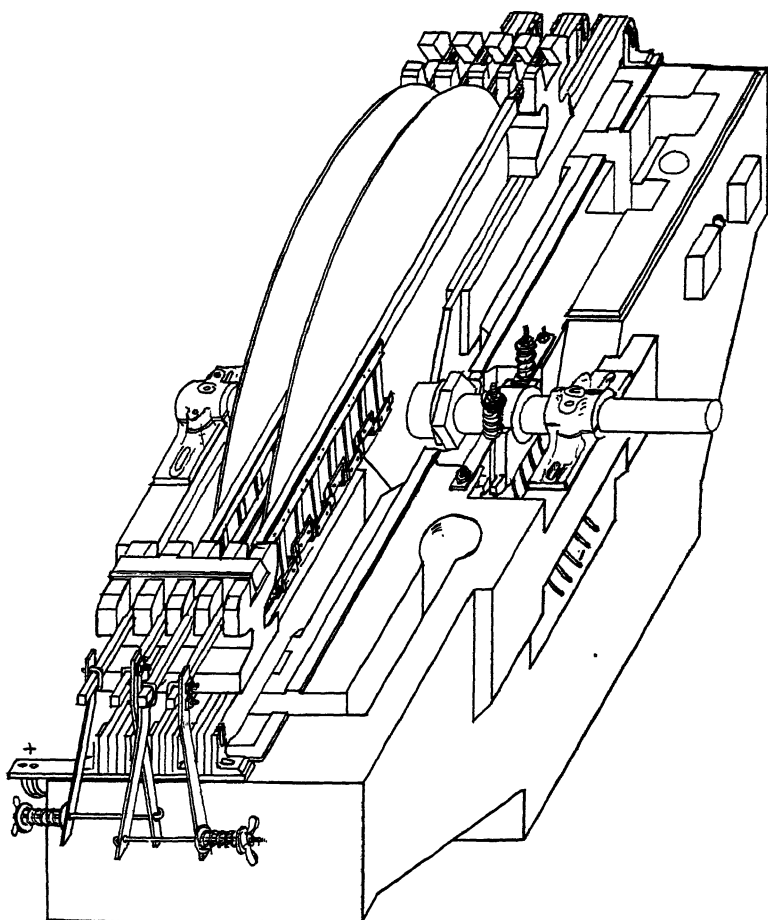
FIG. 14.—48-IN. TWO-CATHODE ELECTROLYTIC IRON CELL, WITHOUT COVER.

In the operation of this cell, the anolyte level is maintained slightly below the level of the catholyte. The level of the latter is maintained by feeding an excess of ferrous chloride solution, which overflows a weir and is then returned in circulation. The level of the anolyte is maintained by a weir, capable of delicate adjustment, which regulates the net withdrawal of anolyte from the cell. A vigorous circulation of anolyte is maintained by means of a steam ejector operating in a well, which takes

the anolyte from one side of the cell and returns it to the other. This serves not only to circulate the anolyte but is also the sole means for maintaining the temperature of the cell.

The operating data of the pilot-plant cell are assembled in Table 14. The current density voltage characteristic of the cell is shown in Fig. 18.
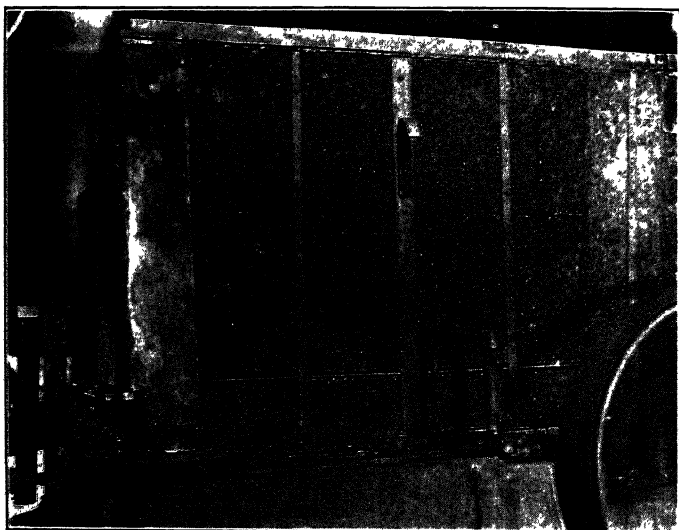
FIG. 15.—COVER OF CELL.

FIG. 16.—DIAPHRAGM.

Some outstanding lessons learned from the operation are summarized as follows:

1. The most economical current density will probably range from 35 to 50 amperes per square foot.

2. When operating at 50 amp. per sq. ft. the temperature of the catholyte should not be less than 80° C. and the anolyte should be at

90° to 95° C. Slightly lower temperatures can be employed at lower current densities, but attempts to operate at room temperature always
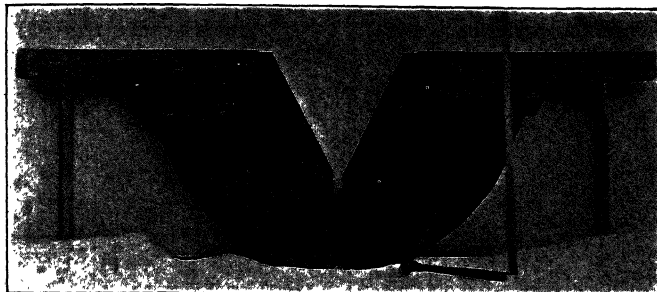
FIG. 17.—ANODE.
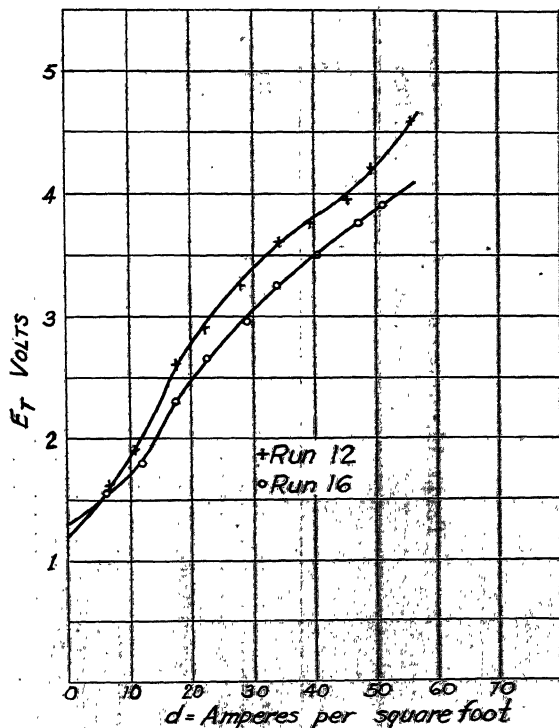
FIG. 18.—POTENTIAL DROP ACROSS 48-IN. IRON CELL WITH GRAPHITE ANODES AND DIAPHRAGMS OF WOVEN ASBESTOS CLOTH.
Voltage given is from end of graphite cross bar to negative slip ring. Add 0.11 volt to get over-all cell voltage.

resulted in cracked deposits. It is also necessary to keep the exposed disks covered with an insulating hood to prevent injury to the deposit.

TABLE 14.—*Summary of Operation of 48-inch Iron Cell*
Sept. 30, 1925 to Jan. 31, 1926

	Run 2 Sept. 30–Oct. 21	Run 6 Nov. 13–Nov. 30	Run 7 Nov. 30–Dec. 5	Run 8 Dec. 5–Dec. 14	Run 9 Dec. 14–Dec. 23	Run 12 Jan. 5–Jan. 15	Run 16 Jan. 25–Jan. 31
Elapsed time, hours	489.5	405	114	220	210.7	236.1	167.3
Time current off, hours	11.08	0.083	None	2.17	1.17	None	0.83
Operating factor, per cent	91.8	99.99	100	99.0	99.4	100	99.5
Average amperes	530	464.5	466	461	923.4	932	939.0
C. D. amp. per sq. ft. submerged area	28.6	25.1	25.2	24.9	49.0	50.3	50.7
Average cell voltage	3.38	3.29	3.42	3.40	4.42	4.11	3.91
Ampere-hours	259000	188110	53024	100450	173452	214400	152680
Theoretical iron production, lb	596.0	432.0	121.9	230.7	308.3	493.5	350.4
Electrolytic iron produced, lb	582.5	413.5	118.5	211.5	394.0	454.5	327.3
Cathodic current efficiency, per cent	97.7	96.0	97.2	91.7	98.9	92.1	93.4
Anodic current efficiency, per cent	88.9	86.5	82.7	85.0	83.2	80.7	78.8
Total kilowatt-hours	876.0	618.9	181.5	341.2	766.7	858.0	604.7
Kw-hr. per lb. elec. iron	1.5	1.46	1.53	1.61	1.95	1.89	1.85
Avg. rate feed to cell, lb. per min	2.88	2.01	2.11	2.28	2.33	2.36	2.46
Avg. rate return circ. of cath. lb. per min	2.19	1.44	1.41	1.44	1.26	1.16	1.23
Avg. rate anolyte outflow, lb. per min	0.74	0.65	0.66	0.78	1.19	1.26	1.27
Avg. temp. feed to preheaters, deg. C						25	29
Avg. temp. feed to cell, deg. C	90.8	100.3	101.7	100.1	93.3	95.9	85.0
Avg. temp. cath. inside, deg. C	77.8	73.0	75.1	78.9	83.2	84.2	81.0

Avg. temp. cath. outside, deg. C	71.8	67.7	66.7	70.7	79.4	76.7	79.0
Avg. temp. anolyte inside, deg. C	88.2	79.5	73.9	80.3	98.4	91.3	96.0
Avg. temp. anolyte outside, deg. C	76.1	71.4	67.4	71.5	91.4	86.9	91.0
Mean cell temperature, deg. C	70.5	73.0	63.3	75.4	88.1	84.8	87.0
Avg. per cent. total iron from filter	12.55	10.84	11.41	10.90	11.94	11.78	12.64
Avg. per cent. total iron feed to cell	10.56	11.83	11.03	10.91	11.34	11.24	11.77
Avg. per cent. ferric iron in feed	0.022	0.031	0.028	0.017	0.003	0.018	0.023
Avg. per cent. total iron in cath. from cell	10.62	11.94	11.09	10.84	11.56	11.11	11.79
Avg. per cent. ferric iron in cath. from cell	0.025	0.036	0.050	0.024	0.000	0.030	0.043
Avg. per cent. total iron in anolyte from cell	8.72	9.71	9.63	9.13	9.40	9.41	9.60
Avg. per cent. ferric iron in anolyte from cell	4.49	5.10	4.17	3.88	4.88	4.81	4.59
Ratio Fe^{+++}/total Fe in anolyte	0.515	0.535	0.433	0.425	0.313	0.511	0.478
Avg. pH of feed	2.46	2.36	2.40	2.65	2.44	2.64	2.60
Normality of H^+ in feed	0.0035	0.0044	0.0046	0.0028	0.0036	0.0023	0.0025
Avg. pH of catholyte		2.88	2.50	2.33	2.36	2.57	2.40
Normality of H^+ in catholyte		0.0048	0.003	0.0048	0.0055	0.0027	0.0040
R.p.m. of cathodes	3	1.8	1.8	1.8	1.8	1.8	1.8
Diaphragm efficiency, per cent	99.5	96.8	100	92.6	93.4	92.8	94.0
Lb. H^+ ion consumed per lb. iron	0.00004	0.00031	0.00031	0.00023	0.00023	0.00071	0.00067
Lb. com'l H_2SO_4 per lb. iron	0.0018	0.014	0.014	0.0104	0.012	0.033	0.031
Total feed per lb. iron				142.2	76.4	73.0	75.4
Net feed per lb. iron				56.2	44.4	43.5	44.2
Ratio ferric produced to iron in feed × 100				16.45	18.00	19.57	18.28
H_2O added as steam to anolyte per lb. Fe				0.90	2.35	1.3	4.55

* Cell voltage is from positive busbar to negative slip ring. Add 0.06 volts to give over-all cell voltage.

3. Dense woven asbestos cloth of chrysotile or crocidolite makes a satisfactory diaphragm, and a practical design has been worked out. The cloth must be closely woven because leakage of Fe^{+++} into the catholyte compartment not only reduces current efficiency but also causes the deposit to crack and peel. The ferric iron in the catholyte should never be more than 0.05 per cent. and it is easy to do better than this (see Table 14).

4. The feed to the cell should be a clear liquor and the hydrogen ion concentration should be carefully controlled at about pH 2.5.

5. Stripping was made possible by heating the cathode starting sheets to give a coating of blue oxide. This gave a sheet which held the deposit successfully during deposition, but permitted removal by a few sharp blows of a hammer.

A large electrolytic iron cell has been designed which embodies the salient features of the pilot-plant cell and which has the following characteristics:

Diameter of cathode disks, in	60
Number of cathodes	12
Current density, amp. per sq. ft	35
Submerged area cathodes	181
Amperes per circuit	6336
Cathodic current efficiency	95
Electrolytic iron produced in 24 hr. continuous operation, lb	331
Voltage across cell terminals	3.48
Gross kw-hr. a.c. per lb. electrolytic iron including excitation and converter losses and power for turning disks	1.97

HEAT REQUIREMENTS OF PROCESS

To extract the values from the sulfide minerals requires hot solutions of ferric chloride. To heat leaching solutions is a costly matter, therefore these solutions should be as concentrated as possible with respect to their content of ferric iron.

High concentration of ferric iron also promotes extraction of values from the minerals. To deposit iron from ferrous chloride solutions and to produce at the same time concentrated anolyte solutions requires a diaphragm cell, and a diaphragm cell for economic reasons demands high current density, and the cell conditions in turn, as shown above, require high temperatures of electrolyte. The condition, therefore, is that boiling temperatures are required in the leaching step and electrodeposition step of the process and, because of the nature of the electrolyte, these temperatures can only be achieved by injecting live steam, which in turn implies the necessity for evaporation to maintain the water balance. Evaporation of ferrous chloride liquors can be accomplished practically only by use of some such device as a disk evaporator of the type employed

in the manufacture of paper pulp, and such an evaporator was employed in the pilot plant.

In view of these facts it becomes of first importance to strike a heat balance of the cell and to estimate the total requirements for fuel. The heat balance of the large cell, which is estimated from the performance of the pilot-plant cell, is given in Table 15.

TABLE 15.—*Calculated Heat Balance of 60-inch 12-cathode Rotating-disk Electrolytic Iron Cell*

Iron plated, .23 lb. per min.

Feed 75 lb. per lb. Fe = 17.3 lb. per min.

Heat In	B.T.U. PER MINUTE
12.55 lb. H_2O in feed at 185° F. above 60°........................	1,570
2.04 lb. Fe in feed at 185° F. above 60°........................	28
2.72 lb. Cl in feed at 185° F. above 60°........................	56
From electrical resistance of 1.97 volts........................	715
Steam required by difference, 1.225 lb. per min. at 40-lb. gage.......	1,284
	3,653

Heat Out	
7.72 lb. H_2O in anolyte at 196° above 60°........................	882
1.255 lb. Fe in anolyte at 196° above 60°........................	17
1.68 lb. Cl in anolyte at 196° above 60°........................	34
5.51 lb. H_2O in catholyte return at 174°........................	628
.87 lb. Fe catholyte return at 174°........................	11
1.26 lb. Cl catholyte return at 174°........................	24
Evaporation of water, 168 lb. per min........................	1,380
Losses to outside through hood and body, 259 sq. ft. external surface at 262 B.t.u. per sq. ft. per min........................	677
	3,653

B.t.u. required in steam per lb. of iron.   (This steam is also employed for circulating the anolyte.) ... 5,580

Gross evaporation per lb. Fe in cell, lb....................... 7.08

Net evaporation from cell circuit equals gross evaporation minus steam introduced, lb.... 1.55

As a result of this and other calculations, it is estimated that total B.t.u. required per lb. electrolytic iron produced in commercial plant = ... 16,450

LOSSES OF CHLORINE

No process of this kind can be carried out without loss of electrolyte, and much consideration was given to this loss in the operation of the pilot plant.   Our conclusion is that the probable losses of chlorine in a large plant are as follows:

	LB. PER LB. ELECTROLYTIC IRON
Filter press cakes and cement copper........................	0.017
Cell circuit solids........................	0.004
Evaporator solids and gases........................	0.011
Loss from iron cell........................	0.038
Total probable loss of chlorine........................	0.070

This loss of chlorine is made up by adding to the electrolyte the required amount of calcium chloride, the calcium of the latter being precipitated as sulfate.

OTHER MEANS OF MAKING ELECTROLYTIC IRON FROM LEACH SOLUTIONS

If the desired end is to produce a dense, nonporous form of electrolytic iron from sulfide ores, iron and steel scrap, or other soluble materials, the authors know of no other method than that described above; but if the raw material available is scrap and if a porous electrolytic iron cathode is satisfactory, which should be the case if the iron is to be remelted, the senior writer has recently developed a much simpler process. In fact, this new process is just as simple in both operation and equipment used as the processes now employed for producing electrolytic copper from suitable ores. By its use, electrolytic iron can be produced very cheaply; so cheaply, in fact, as to make it necessary to demand only a small premium for its extreme purity. Certainly any potential demand for pure iron as such should be encouraged to satisfy itself by the availability of such a process.

New Simplified Process

The purpose of this paper has been primarily to describe our experiments for the production of electrolytic iron from sulfide ores, so no attempt will be made to describe fully the new and simplified process for making electrolytic iron from iron or steel scrap, but a brief outline will be given. The process is based upon the observation that electrolytic iron can be produced under certain conditions at good current efficiency from ferrous chloride electrolytes in simple nondiaphragm cells. These conditions are principally: (1) cell temperature about 25° C.; (2) current density 10 to 15 amp. per sq. ft.; (3) cell effluent containing about 1.25 per cent. ferric iron; (4) cell so constructed that the fresh electrolyte enters at the bottom and flows in a general upward direction through the cell.

Under these conditions, a current efficiency of 70 to 80 per cent. can be realized with a cell voltage of 3.0. The cold cell effluent containing 1.25 per cent. ferric iron is a good solvent for iron scrap and the reduced solution leaving the scrap is easily subjected to the simple steps of purification required before going back to the cell.

By this process the production of pure electrolytic iron is reduced to the lowest possible cost, because any grade of scrap not fit for remelting may be employed. It is suggestive to consider that this electrolytic iron could be melted in induction furnaces and used for producing pure synthetic wrought iron by a recently described process.[25]

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[25] *Blast Furnace & Steel Plant* (1929).

GENERAL CONCLUSIONS

The authors have described in detail a pilot-plant operation for producing iron of almost complete chemical purity and in dense homogeneous form from sulfide ores or materials containing metallic iron. This process requires the use of a cell with diaphragms and a hot electrolyte. When the sulfide ores contain other metals, these are recovered as by-products, and even when copper concentrates are treated, it is necessary to look upon iron as the main product and upon the copper as a secondary product. Also, an outline has been given of a process for producing pure electrolytic iron as porous cathodes from scrap, which employs a simple nondiaphragm cell and a cold electrolyte. Either of these processes is capable of rendering available, on a large scale and at a reasonable cost, iron of almost complete chemical purity, and their commercial development awaits only a greater demand for pure iron.

ACKNOWLEDGMENT

The authors are indebted to the officers and directors of the Engels Copper Mining Co. for financing this work, and particularly to the interest and unfailing cooperation of Mr. George T. Cameron.

DISCUSSION

A. SAUVEUR, Cambridge, Mass.—It is my understanding that a number of years ago Eustis and Perin worked out a method of extracting iron from sulfide ore. Does the method used by these authors differ in any way from that of Eustis and Perin?

R. D. PIKE.—The general flow sheet, that is, the use of an insoluble anode and diaphragm electrolyte and a solution of sulfide, is old. In fact, I thought we covered that thoroughly in the paper and for lack of time I did not mention it in presenting the paper. It was first described by Siemens in 1889. The first people in this country to try out that method were Eustis and Perin, who did work of great value at Milford in the leaching of pyrrhotite and also made a very thorough investigation of the effect of various impurities.

There is no claim for revolutionary invention in this connection. It is a rather old subject. But what had not been done at the time we undertook the work was the development of a practical cell for continuous operation in the production of electrolytic iron, and that together with the flow sheet which is demonstrated in the paper was the work we had to undertake.

MEMBER.—Did your work bring out any data on the cost? There is no cost mentioned in the paper.

R. D. PIKE.—In the general operations involved in the last mentioned process— that is, one in which the iron is supposed to be made from scrap—if you take the scrap free, the general costs must necessarily be similar to those in electrolytic zinc procedure. The mechanical operations and the chemistry are not the same, but they are rather closely similar, and in the sulfide process there are yet so many unknown factors as to the depreciation of the materials in operating with ferric chloride liquors at boiling points that we do not like to feel that we know much about costs except theoretically. In the other process, where the solutions are cold, there need

be expected no depreciation of materials beyond what would be obtained in many similar plants.

R. MOLDENKE, Watchung, N. J.—Did you try this porous material under high temperature, in its further manipulation? If so, what did you get? The reason I ask is that I had some experience with heating iron sponge in Germany, and found that the oxidation was so great that the results were worthless. Only after applying very high pressures, to compress the spongy mass into more solid cakes, could the material be heated hot enough to forge out well, and no oxidation was indicated.

R. D. PIKE.—It is not porous like sponge iron but is a regular deposit of iron, with numerous "hydrogen" holes more or less perpendicular to the plane of deposition.

C. G. MAIER, Berkeley, Calif. (written discussion).—The authors of this paper deserve great commendation for their publication of this explicit résumé of experimental data of a sort that would ordinarily have remained buried in obsolete business files. The general conclusion that "when sulfide ores contain other metals" (presumably other than iron) "it is necessary to look upon iron as the main product" will come as a startling statement to many who have been interested in the hydrometallurgy of copper. The logic leading to the conclusion that such a material as Walker concentrate, containing at least $50 worth of copper per ton, and not more than $5 or $6 possible value of iron, is an "iron ore" seems obscure, unless it be merely the implied admission that, even in boiling solutions, the extraction of copper was poor!

One hesitates to reiterate the statement, usually considered axiomatic by copper metallurgists, that no copper-leaching process can hope to succeed unless it can make a better extraction, at no greater cost, than normal smelting. To leach special ores, such as partly oxidized ones, fills a definite metallurgical need. The authors somewhat casually dismiss in a single paragraph the "second leaching," whereby extractions "over 99 per cent." are obtained. The composition of the material wasted for the second leaching is not given, but from other figures may be estimated to be approximately 9.7 per cent. Cu, 35.1 per cent. S, 22.8 per cent. Fe, 32.4 per cent. insol. To obtain high extraction on such material by roasting and leaching is much simpler in a Hoskins furnace than in an operating plant. There remains to be emphasized the rather obvious fact that the copper in this process is recovered as cement copper, which would either have to be retreated by electrolytic methods or sent to the copper converter. It is usually considered unprofitable to make electrolytic copper from cement on a small scale, and the converting cost is no small proportion of the smelting cost.

These considerations do not, however, detract from the fact that these authors have done a valuable piece of work in producing electrolytic iron. The "metal" metallurgist has had pure copper for 30 years or more, pure zinc quite recently, but truly pure iron seems just ahead. It seems probable, however, that the supply of pure iron must precede a general market, a condition that will ensue when some process, the economic justification of which lies elsewhere, *must* inherently produce pure iron. That, at least, is the lesson of high-purity metals from the past. This sulfide process is also a "noble experiment."

R. D. PIKE (written discussion).—Replying to Mr. Maier, there is much in the viewpoint which obtains when a research starts. Our viewpoint at that time was that we would produce 1½ to 2 lb. of pure electrolytic iron per pound of copper as a by-product of a process for recovering the latter in the form of cement copper from its concentrates. As we expected to get about five cents per pound for the iron, this viewpoint seemed to be sound. When the research had been completed and the data finally digested, it was perceived that the electrolytic iron "tail" had very

violently "wagged" the copper dog. It became apparent that the important and primary feature of the process was the manufacture of electrolytic iron. The by-product consisted of certain services of more or less doubtful value rendered in the way of transforming the copper in the form of concentrates to copper in the form of cement copper. This pointed to the conclusion that the proper raw material for the process is not copper concentrates, but pyrrhotites with marginal values of copper and possibly other metals. The new viewpoint following from this conclusion places the process in its proper economic perspective. We now understand that pure iron cathodes in the excellent nonporous form, which are produced by the process, must carry practically all of the burden of the cost, and at this writing no market demand has made itself apparent, which would justify their manufacture. Possibly some such demand may make itself felt in the future. There is no call either for optimism or pessimism. It is simply desirable to record the facts, and to get them in proper perspective.

In an argument, the last word is often decisive. So in a research, the last idea is apt to carry the most value. I feel that possibly something of this kind may have happened here in relation to my proposal for making a somewhat porous, though pure, iron cathode in simple nondiaphragm cells from cold electrolytes. It may be suggestive to consider that one could start with pyrite or pyrrhotite roast, reduce the cinders to sponge iron, and then dissolve the latter, which can be done very readily in the cold dilute ferric leach from the electrolytic iron cells. In this way a high recovery would be made of both the iron and marginal metals, the plant would be relatively inexpensive and the process simple. Possibly situations might be found where sulfuric acid could be marketed. It also seems possible that such a process could be worked economically under certain favorable conditions, provided a market existed for the iron cathodes at around $3\frac{1}{2}$ to 4 c. per pound.

So far as I know, no such market exists. Some day a demand may arise for ferrous products, which would be melted in high-frequency induction furnaces *in vacuo*. Such products would be absolutely controlled as to analysis, would be melted in absolutely refractory crucibles, would be free from gases and from metals and metalloids except those intentionally added. If the demand ever arises for such products in quantity the iron of desired purity can be made available at moderate cost.

[A discussion by T. D. Yensen, with a reply by R. D. Pike, was published in *Mining and Metallurgy*, April, 1930, page 216.]

Sintering Limonitic Iron Ores at Ironton, Minnesota*

BY PERRY G. HARRISON,† IRONTON, MINN.

THE mixing of fine ores with fuel and burning under induced draft is called sintering in iron-ore practice and either sintering or roasting in copper and lead metallurgy.

The first development of sintering was the Huntington-Heberlein process, in which fine sulfide ores mixed with fuel were charged into a pot and burned under the action of an upcast current of air introduced at the bottom of the pot. Modern development has resulted in two types of machine; the continuous Dwight-Lloyd machine, which consists of heat-resisting grates and a moving beltlike type of hearth constructed of metal, in which air is drawn downward through the bed, and the stationary Greenawalt batch process, which operates in the same manner as the Dwight-Lloyd except that the hearth is stationary.

The recent rapid increase in the use of sintering has been the result of two great advances in metallurgical process—flotation and the treatment of flue dust. The Dwight-Lloyd machine is used in many plants for agglomerating flotation concentrates and at the same time reducing the sulfur content to furnace requirements and it has become standard practice to treat iron blast-furnace flue dust by either the Greenawalt or Dwight-Lloyd machine, so that it can be recharged into the furnace.

The mining of low-grade magnetite iron deposits and their beneficiating by grinding and magnetic separation resulted in a fine concentrate extremely detrimental to blast-furnace practice. These concentrates are sintered and made into ideal material for blast-furnace use. Incidentally, coke savings of about 400 lb. per ton of pig are reported.

SINTERING AT EVERGREEN PLANT

The application to limonitic iron ores is the most recent development of the sintering process. The first plant in the Lake Superior region was erected by the Minnesota Sintering Co., a subsidiary of the Evergreen Mining Co., at Ironton, Minn., in 1924. This plant was designed to treat Cuyuna Range iron and manganiferous ores containing low silica, high moisture and a structure objectionable because of a large proportion

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* Address given by the author before the Minnesota Section of the Institute, Dec. 9, 1929.

† General Manager, Evergreen Mining Co.

of fines.   Ores of this quality constitute approximately one-half of the ore reserve in the Evergreen mine.

Until 1928 operations of this plant were largely in the experimental state and by reason of the drop in ore prices at about the time the plant was ready for operation and the restricted demand for ores for the next years, sufficient outlet for the plant was not obtained to demonstrate whether or not sintering had a commercial possibility.   However, in 1928 this plant produced 115,000 tons of iron and manganiferous sinters on a Dwight-Lloyd machine size 42 in. by 64 ft.   Sufficient information was obtained by this operation to indicate that operating costs on a machine of this capacity, when coupled with ore prices current during that year, were prohibitive.

Satisfactory reduction in sintering costs had been obtained, however, at both Buffalo and Chateauguay by the replacement of 42-in. Dwight-Lloyd sintering machines by machines with a 72-in. hearth width.   On the basis of these results, and estimated savings calculated by the operators of the Evergreen plant, the plant was rebuilt during the winter of 1928–29, with most satisfactory results, as indicated in Table 1.   These figures apply to the entire crushing, screening and sintering operation of the plant.   A general view of the plant is shown in Fig. 1.

TABLE 1.—*Operating Results at Evergreen Plant*
SINTER PRODUCTION RATE

Year	Tonnage	Actual Hours Operated	Tons per Actual Hour Operated	Square Feet Effective Grate Area	Tons per 24 Hours per Square Foot Grate Area
1926	15,784	921	17.14	224	1.84
1927	19,794	1,038	19.07	224	2.04
1928	115,546	5,054	22.86	224	2.45
1929	213,022	4,826	44.14	452	2.34

POWER COST COMPARISON

		PER TON SINTER
1928	42 in. by 64 ft. Dwight-Lloyd sintering machine.....	$0.2179
1929	72 in. by 76 ft. Dwight-Lloyd sintering machine.....	0.1443

LABOR EFFICIENCY COMPARISON

		TONS SINTER PER MAN SHIFT
1928	42-in. by 64 ft. Dwight-Lloyd sintering machine....	11.86
1929	72-in. by 76-ft. Dwight-Lloyd sintering machine....	16.77

The Flow Sheet

The flow sheet of the present Evergreen plant is shown in Fig. 2. Roughly, the plant is divided into four sections: the primary screening

and crushing section, the fine-ore screening and crushing and washing section, the fuel-crushing section and the sintering-machine section.

Crude ore and fuel are received at the plant in standard-gage hopper-bottom cars, which are spotted on tail tracks having 1.5 per cent. grade. The cars are moved by gravity through the plant; first over a chain grizzly, where they are dumped, and then underneath reloading chutes, where they are loaded with either sinter or coarse ore for shipment to the docks at Superior.

The chain grizzly, built by the National Iron Co. of Duluth, is 50 in. wide by 33 ft. long; the chains are set to pass all material less than 2½ in. in size. The undersize falls directly into storage bins; the oversize is carried by the moving chains to a 24 by 36-in. Buchanan crusher break-
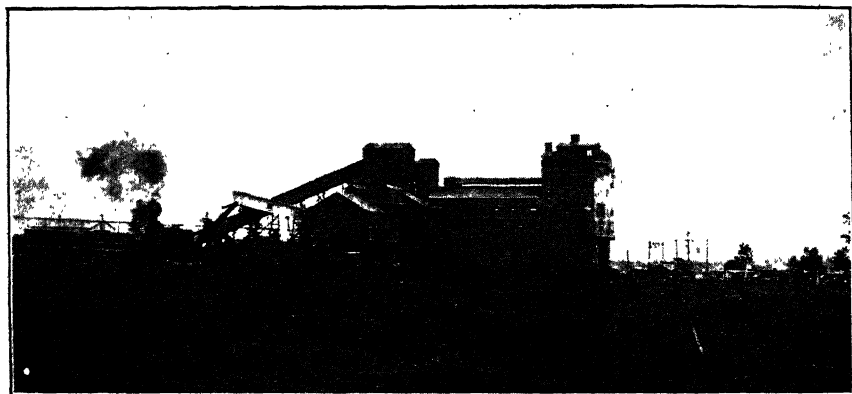
FIG. 1.—GENERAL VIEW OF EVERGREEN PLANT.

ing to 4 in. The crushed material and fines are recombined on an inclined 30-in. conveyor passing over a Merrick weightometer, where the weight of all material entering the plant is recorded, and thence are elevated to the top of the screening section of the plant.

This inclined conveyor discharges into a three-way hopper, so that the ore can be spouted either directly out of the plant and into ore cars or into a small ore-washing adjunct to the plant, or be passed over a bank of vibrating screens; also, when fuel is being handled, the discharge can be made into coarse-fuel bins. Ore is delivered to the vibrating screens through a swinging spout and the fines (material of −⅜-in. mesh) are conveyed directly to the storage bins for the sintering machines. The oversize of the screens can be spouted out of the plant and into ore cars for direct shipment or can be conveyed to a Dixie hammer mill equipped with a moving breaker plate set to crush to about ⅜ in. This mill is designed to handle sticky ore. The discharge of this crusher is returned to the main stream of material entering the plant over the 30-in. inclined conveyor and is rescreened.

There are five 70-ton fine-ore storage bins, which are arranged to discharge by means of accurately controlled revolving disk feeders on to a collector conveyor. This installation makes possible a mixing of various ores so as to control final sinter analyses, in a manner similar to cement practice.
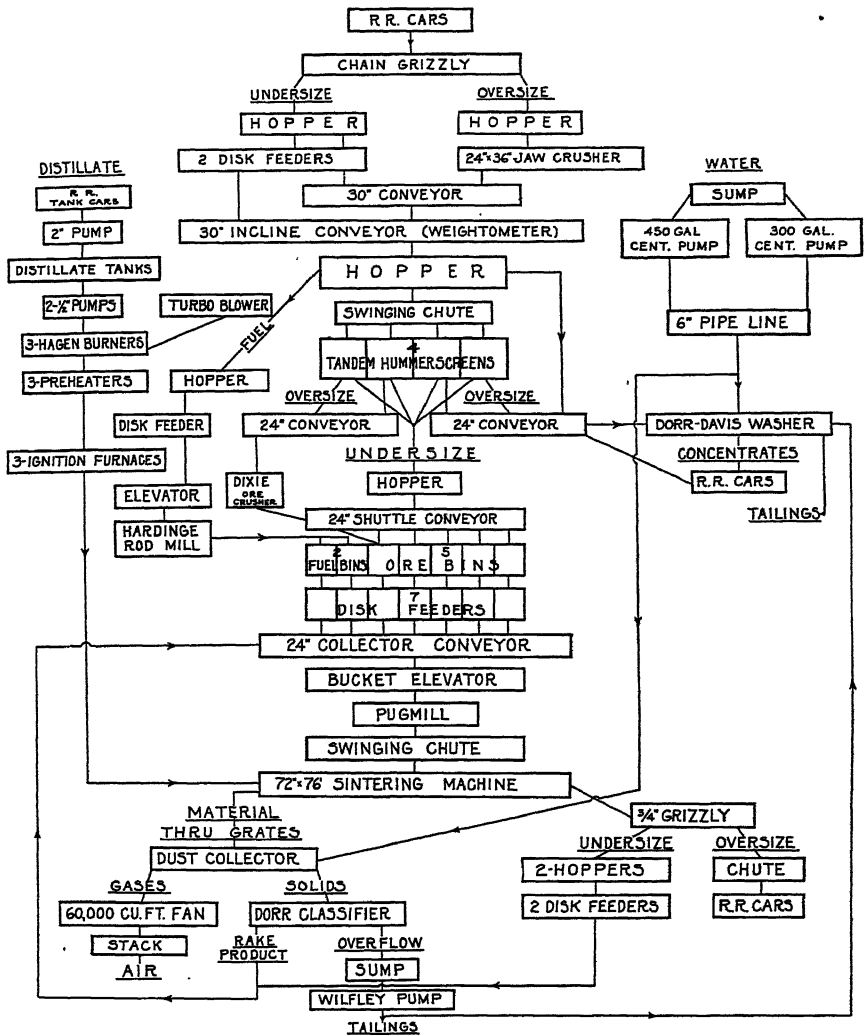
FIG. 2.—FLOW SHEET, EVERGREEN PLANT.

Fuel entering the plant and stored in the coarse-fuel bins is conveyed to and crushed in a Hardinge rod mill 5 ft. dia. by 10 ft. long, grinding to −15 mesh. The crushed fuel is conveyed to two 70-ton storage bins located in line with and feeding on to the same collector conveyor that serves the fine-ore bins.

Ore, fuel and fine sinter screened from the discharge of the sintering machine are conveyed by the collector conveyor to an elevator and raised to the top of the sintering plant, where they are discharged into a drum-type pug mill especially designed to handle the sticky, abrasive material treated in this plant. In the pug mill, the ore, fuel, return sinter and some additional water are mixed to the consistency required by the sintering operation. The discharge from the pug mill is spouted to the head end of the sintering machine through a swinging spout and hopper, which allow the material being delivered to the machine to fall over an inclined surface of material previously delivered so that the coarse material may segregate out toward the bottom of the sinter bed.

The moving sinter bed carries the mixture of ore, fuel and returned sinter to three ignition furnaces. Each furnace covers the width of the bed and burns gas obtained by treating in preheating retorts oil of 38° gravity.

Ignition of the solid fuel in the upper portion of the bed of material takes place under these furnaces and the burning zone gradually travels downward through the bed under the influence of a downcast draft of air drawn through the bed by a Buffalo Forge Co. fan, which furnishes 60,000 cu. ft. per min. and operates at from 15 to 18 in. of water vacuum. By the time the material in the bed has traveled 76 ft. and reached the discharge end of the machine, the zone of burning and incipient fusion— *i. e.*, sintering—has burned completely through the bed. The finished sinter, ranging in size from fines to large chunks 2 ft. wide by 6 ft. long and about 1 ft. thick, drop off the bed and discharge on to a grizzly made of railroad steel set 1¼ in. apart; there any fine sinter or unsintered ore drops through into the bin for return sinter and the coarse material is spouted into railroad cars, which are protected from the red hot material by water sprays arranged to cool the part of the material that is close to the sides of the car.

The flow sheet of the plant is extremely flexible. Ore delivered to the plant can be treated as follows: (1) it can be simply crushed and reloaded into railroad cars; (2) it can be crushed and the fines screened out and sintered while the coarse is loaded for shipment direct, or washed and the coarse material, reduced in silica and moisture, can be shipped; (3) the entire ore can be crushed and washed; (4) the entire ore can be crushed to pass ⅜-in. mesh and sintered. This wide flexibility makes possible the beneficiation of greatly varying types of ore.

Metallurgical Results in 1929

The metallurgical results obtained on ore put through the sintering process during 1929 are shown in Table 2.

TABLE 2.—*Evergreen Sinter Metallurgy during* 1929

IRON ORE

	Tons	Iron Per Cent.	Phosphorus Per Cent.	Silicon Per Cent.	Manganese Per Cent.	Aluminum Per Cent.	Loss Per Cent.	Moisture Per Cent.	F.O.B. Mine Value Per Ton Product
Crude ore to plant.........	249,790								
Dried..................		53.08	0.275	8.76	1.09	4.04	7.61		
Natural...............		44.95	0.233	7.42	0.92	3.42	6.44 Gain	15.32	
Sinter shipped............	192,477								
Dried..................		59.20	0.322	9.48	1.19	5.23	1.15		
Natural...............		58.89	0.320	9.43	1.18	5.20	1.14	0.50	
Recovery...............	77.1%								
Extraction..............		100.9	105.8	97.9	98.8	117.2	Nil	2.5	
Ratio of natural analyses		1.31	1.37	1.27	1.28	1.52		0.03	

Theoretical value of crude ore (too low grade to actually sell)

```
  44.95 @0.08738.............................  $3.93 Mesabi Non-Bessemer
   4.55   0.08738.............................   0.40 Penalty
                                                 ‾‾‾‾
                                                 3.53
                                                 1.79 Freight            $1.74
Sinter value 58.89 @0.08738.............................  $5.15
                                                           1.79 Freight   3.36
                                                                         ‾‾‾‾‾
Increase in F.O.B. Mine Value Due to Sintering                           $1.62
```

MANGANESE ORE

	Tons	Iron Per Cent.	Phosphorus Per Cent.	Silicon Per Cent.	Manganese Per Cent.	Aluminum Per Cent.	Loss Per Cent.	Moisture Per Cent.	F.O.B. Mine Value Per Ton Product
Crude ore to plant.........	27,216								
Dried..................		45.81	0.342	9.69	4.13	5.02	10.84		
Natural...............		37.60	0.281	7.95	3.39	4.12	8.90 Gain	17.92	
Sinter shipped............	19,659								
Dried..................		53.08	0.435	10.83	4.74	5.64	1.10		
Natural...............		52.81	0.433	10.77	4.72	5.61	1.09	0.50	
Recovery...............	72.2%								
Extraction..............		101.5	111.7	97.9	100.6	98.3	Nil	2.0	
Ratio of natural analyses		1.40	1.54	1.35	1.39	1.36		0.03	

Theoretical value of crude ore (too low grade to actually sell)

```
  37.60
   3.39
  ‾‾‾‾‾
  40.99 @ 0.09029.........................  $3.70 Old Range Non-Bessemer
                                            1.79 Freight            $1.91
Sinter value 52.81
             4.72
            ‾‾‾‾‾
            57.53   0.09029.........................  $5.19
                                                      1.79 Freight   3.40
                                                                    ‾‾‾‾‾
Increase in F.O.B. Mine Value Due to Sintering                      $1.49
```

Sinter as produced by the Evergreen Mining Co. is very coarse, but it is subjected to a drop of about 60 ft. in loading from dock to boat, which breaks down the large lumps and leaves a firm, rugged product that will not break down further under load although it still retains a cellular and porous structure, which, like coke, permits the free and uniform distribution and passage of furnace gases with consequent good reducibility and freedom from hangs and slips in the blast furnace.

Although both cellular and porous, Evergreen sinter, being vitreous, will not absorb water and therefore will not freeze in stock pile. An interesting example of this was the loading, in subzero weather, of the last boat to leave the head of the lakes with sinter this year, in less than three hours.

Sinter Screen Analysis

Report of mesh tests taken by Crowell and Murray at port of delivery on 29 cargoes of sinter delivered during 1929 is given in Table 3.

TABLE 3.—*Mesh Tests on 29 Cargoes of Sinter*

	PER CENT.	ACCUMU-LATIVE, PER CENT.
+ 1 in.	25.54	
+ ½ in., through 1 in.	20.00	
+ ¼ in., through ½ in.	26.45	
+ ⅛ in., through ¼ in.	15.42	87.41
+ 20 mesh, through ⅛ in.	8.27	95.68
+ 40 mesh, through 20 mesh	2.57	
+ 60 mesh, through 40 mesh	0.66	
+ 80 mesh, through 60 mesh	0.21	
+100 mesh, through 80 mesh	0.16	
Passing 100 mesh 0.72 per cent.	3.60	99.28

During 1929, and for the particular purpose of improving the screen test of ore of direct shipping grade that was somewhat objectionable in furnace practice by reason of fines, a varying proportion of the ore was sent to the plant, the coarse ore was screened out and the fines were sintered and recombined in the dock with the crude ore forming the bulk of the shipments. The sharply improved screen tests obtained with increased amounts of screened coarse ore and sinter are shown in Table 4. The table shows the actual mixing experience of 1929 and also the expected screen test if all of the ore were screened and the resultant (about 50 per cent.) coarse ore were mixed with the sintered fines.

Incidentally the admixture of small amounts of sinter, particularly if crushed through 2½-in. opening, with crude ore admits an easy method of control of grading, as the high natural analysis of the sinter will quickly allow the grading out of crude ore material slightly below contract grade without material variation in the ratio of metallic contents to silica,

alumina and phosphorus; the only essential difference between sinter and the crude ore from which it is made being the elimination of water. The materials—coarse ore and crushed sinter—mix beautifully, as their screen test is similar and coarse screened ore is superficially dry, as is sinter.

TABLE 4.—*Improvement in Screen Test on Identical Ore Caused by Screening and Sintering of Fines during 1929*

	Actual Iron Ore Shipped					Expectation 100 Per Cent. Beneficiated, Per Cent.
	Group 1, 1928	Group 2	Group 3	Group 4	Group 5	
Tons Shipped	41,618	12,024	16,819	15,762	5,714	
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
Preparation:						
None...............	100.0	94.8	83.3	72.3	52.1	0.0
Screened coarse......		5.2	6.2	15.9	27.2	50.0
Sintered fines........		0.0	10.5	18.6	20.7	50.0
Beneficiated.........		5.2	16.7	34.5	47.9	100.0
Screen Test						
+ ⅛ in............	46.5	51.5	62.3	58.5	68.2	80.4
+ 20 mesh.........	17.3	13.9	12.6	14.5	12.9	9.8
+ 40 mesh.........	14.2	12.4	8.3	10.9	8.7	4.7
+ 60 mesh.........	6.6	6.9	4.5	4.9	3.2	2.2
+ 80 mesh.........	1.5	1.6	1.1	1.1	.6	.6
+100 mesh.........	3.0	3.2	2.0	1.9	1.2	.6
−100 mesh.........	10.9	10.5	9.2	8.2	5.2	1.7
Total...............	100.0	100.0	100.0	100.0	100.0	100.0

COST OF SINTERING IRON ORE

As compared to washing, or washing and jigging, of iron ores, the sintering process is expensive. The application of the process to limonitic iron ores by The Evergreen Mining Co. is too new to establish a cost structure that can be expected to be permanent. This is evidenced by the fact that the cost of sintering was cut $0.41 per ton by improvements to plant, capacity and methods from 1928 operations to 1929; also by the fact that as extensive a program of plant improvement and enlargement is scheduled for the current winter as was put through the ·last winter, including the lengthening of the sinter machine to 127 ft., which will result in 762 sq. ft. of grate area, or a machine one-third larger than the largest 96-ft. sintering machines now being erected by the Bethlehem Steel Corpn. Despite all accomplished and hoped for cost reductions, the process is likely to have its application confined to ores which by reason of structure or analysis are difficultly merchantable in

their natural state and which are unsuitable to water concentration because the fines are high in iron.   Effective beneficiation of iron ores by th ewashing process can be accomplished only with ores in which the fines, being the bulk of the material removed, are high in silica and low in iron.   The field for sintering, however, remains fairly large, particularly applied to ores under the disability of double unit penalties or on which freight costs per unit of metallic material are high.   An example of this is given in Table 5.

TABLE 5.—*Freight Advantages Due to Sintering*

FREIGHT ADVANTAGE TO OPERATOR
Extreme Case; *i. e.* Cuyuna Manganiferous Ore

	Combined Iron and Manganese, Per Cent.	Freight to Lake Erie Port	
		Per Ton	Per Unit
Average Cuyuna Range manganiferous ore...	44.00	1.79	0.04069
Resultant sinter.........................	57.00	1.79	0.03140
ADVANTAGE, 57.00 × 0.00929..............		$0.53	0.00929

FREIGHT ADVANTAGE TO PURCHASER
Interior Furnace—Pittsburgh

	Combined Iron and Manganese, Per Cent.	Freight to Pittsburgh	
		Per Ton	Per Unit
Average Cuyuna Range manganiferous ore...	44.00	1.23	0.02795
Resultant sinter.........................	57.00	1.23	0.02158
ADVANTAGE, 57.00 × 0.00637..............		$0.36	0.00637
TOTAL FREIGHT ADVANTAGE MINE TO PITTSBURGH...........................		$0.89	

While the sintering of iron ores is restricted by cost, for the present at least, to ores objectionable, or under double unit penalties, because of low natural metallic content, there seems to be a possibility of a much greater field.   The blast-furnace operator spends time, energy and money in order to assure himself of a supply of both coke and limestone sized and as nearly as possible free of fines, then dumps into the furnace great quantities of potential flue dust, in the form of soft, fine iron ores. This chokes up the operation and results in required high blast pressures, retarded driving rate and high losses in dust that has to be expensively reclaimed, sintered and recharged into the furnace.

Practically all Mesabi ores are crushed.   These ores could also be screened over possibly ¼-in. screens at only slightly increased cost.   The

fines, probably around 30 per cent., if then sintered and recombined with the coarse ore would give the blast-furnace operator an ore with the high driving rate of a limonitic hematite and a structure practically free from choking flue-dust-forming fines. A suggestion for the beneficiation of Mesabi ore is given in Table 6.

TABLE 6.—*Theoretical Beneficiation of Average Mesabi Ore*

	Units	Iron, Per Cent.	Phosphorus, Per Cent.	Silicon, Per Cent.	Manganese, Per Cent.	Loss, Per Cent.	Moisture, Per Cent.
Crude ore................	10,000						
Dried................		58.50	0.076	7.86	0.79	6.04	
Natural...............		50.80	0.066	6.83	0.69	5.25	13.16
							18.41 Water

				Per Cent.			
To Sinter..............	3,000	Loss on ignition, ore		6.04		1.15	Sinter gain on ignition
@ 80.44% Recovery		Gain on ignition					
		sinter..........		1.16		19.56	Total loss
				7.20		80.44	Tonnage recovery
		Divide analyses by 92.80					
		Allow fuel ash 0.50 silica dilution					
						Gain	
		63.04	.082	8.98	.85	1.16	
Sinter..................	2,413	62.72	.082	8.93	.85	1.15	.50
						Loss	
		58.50	.076	7.86	.79	6.04	
Coarse ore..............	6,869	51.77	.067	6.96	.70	5.35	11.50
		59.79	.078	8.18	.81	4.01	
Resultant mix...........	9,282	54.62	.071	7.47	.74	3.66	8.64

The resultant mix ore indicated in the table would probably have less than 2 per cent. fines passing 100 mesh and its use should result in materially lowered blast-furnace costs and losses.

If such a Mesabi ore is worth and can command a premium only slightly greater than is currently obtained for old range ores, it can be produced commercially, and there will result a much greater field for sintering than if the process is restricted to the beneficiation of off-grade or nonmerchantable ores.

DISCUSSION

H. J. ALLEN, Cleveland, Ohio.—Your sinter screen tests are taken at the mine or at the lower lake ports?

P. G. HARRISON.—They are taken at lower lake ports at point of delivery by Crowell & Murray. The ones taken at our mine have no significance at all—they would show 10 times as much in the coarse sizes.

R. H. SWEETSER, Columbus, Ohio.—I want to ask about the fuel that is used.

P. G. HARRISON.—We have used Pocahontas screenings, anthracite dust, and we are now using ground coke breeze. We grind it, and it is rather a difficult problem. Coke breeze in itself is not hard to break up, but when it is used in connection with

a soft ore, there is a tendency for the coke to pack and set in the soft ore, like carbon in a drill bit, causing excessive wear on all surfaces. Hammer-mill hammers go to pieces against it. At present we are using coke breeze, 11 per cent. That probably is very high in relation to the experience of most of you. However, we have to put about 1300 or 1400 tons of material on our sinter bed to get 1000 tons off. Flue dust has only superficial moisture and you are driving off only 10 per cent. of the material. We are driving off 22 to 30 per cent. of the material. The loss in weight is one reason that makes the fuel required high; the other is that we also have the necessity of evaporating all that water. It takes additional fuel.

R. H. SWEETSER.—One more question. The paper speaks of the sinter as vitreous. If anything is vitreous in sinter, it means that a very high heat has been used. I wonder if 11 per cent. fuel heat is not too high and if you really mean "vitreous."

P. G. HARRISON.—I really mean vitreous. During the days when we were doing considerable experimenting and not moving our product to any definite customer, about 1350 tons of sinter were stacked. In January, at some 30° below zero, we moved all that material without blasting. In other words, it had not absorbed water. Incidentally, our average moisture analysis at lower lake points is, I think, 0.4 per cent., showing that there is no moisture absorbed from the upper lake ports to the lower lake ports.

Mr. Schwartz last year announced that not only is there incipient fusion,[1] but actual fusion and recrystallization of the iron ore particles, in sinter. That, according to his work, is characteristic of all sinters.

G. B. WATERHOUSE, Cambridge, Mass.—One member here hopes that something will be said about the advantages of using sinter in blast-furnace work, if we can devote a few minutes to that.

T. L. JOSEPH, Minneapolis, Minn.—The U. S. Bureau of Mines attempted to find out something about what goes on in the interior of an iron blast furnace. During the course of this investigation, holes were drilled in the sides of several furnaces and, by means of water-cooled tubes, the conditions existing in the charge were surveyed. Some very large irregularities were found from furnace to furnace and also across a particular plane or level of an individual furnace.

The blast furnace, as we all know, is an operation based primarily on the counter-current movement of solids and gases. It is a difficult mechanical problem to move large quantities of fine Mesabi ore countercurrent to a large volume of ascending gases. The blast-furnace men have worked out the best methods of filling to permit regular settling of the charge and also permit the most advantageous operation from other standpoints. We found, however, that the extent of preparation in the shaft varied a great deal from furnace to furnace, due primarily to the difficulty of getting gases to percolate uniformly through a mass of fine iron ore and coke.

For example, a furnace operating in Utah had reduced 96 per cent. of the ore at a level approximately at the top of bosh. Another furnace in the southern district had reduced about 80 per cent. of the ore at the top of bosh. A furnace in the Chicago district operating on lake ores had reduced only about 25 per cent. of the ore at the same level.

The blast furnace is 80 to 90 ft. tall. Most of that furnace is devoted to this preparation of the material before it reaches the hearth. We have felt that sintering is a step in the right direction towards improving the upper 70 ft. of the blast furnace.

[1] G. M. Schwartz: Iron-ore Sinter. *Trans.* A. I. M. E., Iron and Steel Div. (1929) 63.

However, I think that as more sinter is used it is going to be necessary to modify methods of filling slightly. Suppose you put on 50 per cent. of sinter. The volume of that charge is increased by the porosity of the sinter, and it means that the average size of the particles in a charge has been materially changed. Some people may be slightly disappointed in sinter because of the difficulty of working out a sequence of filling to take account of the difference in the size of sinter and crude ore. But I think it can be done and it certainly seems a step in the right direction.

Concentration of the Mesabi Hematites

By E. W. Davis,* Minneapolis, Minn.

THE large iron-ore producers on the Mesabi Range are able to maintain the silica in their shipping products at from 8 to 10 per cent. by mixing ores of various grades, some assaying 4 per cent. silica and some as high as 18 per cent. silica. For each ton of 4 per cent. silica ore mined, a ton of 14 per cent. silica ore can be mined and mixed with it and the average grade maintained at 9 per cent. This mixing operation has made possible the utilization of large quantities of ore too lean to be used alone, and herein lies the advantage of the producers who operate a number of mines at the same time. As the grade of the ore from one of the properties falls off, a little high-grade ore from another property can be mixed with it and the average maintained, while if one property alone were being operated all of the ore below grade would be left behind.

This mixing operation, however, can continue only as long as there is high-grade ore available for mixing with the high-silica ores and, while the tonnage of iron ore in the Mesabi Range is still enormous, the tonnage of high-grade ore suitable for mixing with any quantity of low-grade ore is being rapidly depleted. Obviously, if an 18 per cent. silica ore can be reduced by concentration methods to 12 per cent. silica, considerably more of it can be utilized with a given amount of high-grade ore. The operators on the Mesabi Range recognize this situation and are energetically endeavoring to reduce the silica in their concentration plants because every unit of silica that can be removed by concentration is a conservation of their high-grade ores.

More Elaborate Processes Will Be Needed

At the present time there are thirty-seven concentrating plants on the Mesabi Range, and about one-third of the total ore shipped is beneficiated in these plants. In about one-half of these plants no reduction is made in the silica but the moisture or structure of the ore is improved. The washing process is by far the most important method for the removal of silica, and it is interesting to observe that the tonnage of "wash" ore during the past five years has shown practically no increase although the total tonnage of ore shipped has increased. This is due to the fact that the available tonnage of wash ore is being depleted and the amount

of true wash ore left is comparatively small. In the past, a wash ore was classified as material that would produce a 6 or 8 per cent. silica concentrate after washing, but now many washing plants are producing concentrates assaying 10 to 12 per cent. silica. It is evident, therefore, that in spite of the large tonnage of ore that is being beneficiated each year, the rapidly disappearing high-grade ore mines must still carry the burden of the demand, and the burden on these mines has declined little if any during the past five years.

All of this leads to the conclusion that more elaborate beneficiating processes must be used eventually for the production of low-silica concentrate from the rocky wash and lean ores. These processes in various degrees of perfection are available but at the present time many difficulties stand in the way of their usefulness. From a technical standpoint, the irregularity of the structure and analyses of the ore causes considerable difficulty and, from a financial standpoint, the high first cost of plants for treating this low-grade material is discouraging. In addition to this, operating costs on more elaborate plants will be higher than at present and the actual profit on iron ore is so small now that operating costs cannot be allowed to advance until there is an advance in the price of iron ore. The processes that will succeed in the treatment of this low-grade material will be those that will take ore of difficult structures, moistures and analyses and from them produce uniform low-silica high-iron concentrate suitable for blast-furnace use with a total plant-operating expense not much in excess of $1 per ton of concentrate. This would not be difficult if it were not for the fact that fine grinding undoubtedly will be required and a considerable amount of fine concentrate will be produced that must be sintered. This sintering cost alone will amount to about $1 per ton of sinter, therefore it is apparent that a considerable proportion of the concentrate produced must be sufficiently coarse to eliminate the necessity for sintering this portion of the ore.

Without going further into the discussion of plants and processes, the following generalizations on the beneficiation of low-grade Mesabi ores are presented with the understanding that the statements are subject to modification through new developments in the field of ore dressing and changes in the price of iron ore:

1. The concentrate produced should contain 9 per cent. or less silica and 60 per cent. or more iron.

2. The recovery of iron should be above 85 per cent.

3. At least one-half of the concentrate should require no sintering.

4. Radical changes in structure and analyses of the ore should not seriously affect the grade of concentrate produced.

5. The plant should be at some central point so that its ore supply will come from a number of mines with a long total operating life.

6. The plant should be capable of expansion in size to produce at least 1,000,000 tons of concentrate during a shipping season.

7. The total cost of treatment cannot greatly exceed $1 per ton of ore shipped, with the present price of iron ore.

The necessity for treating ores of varying analyses and structures would indicate that future plants would consist of crushers and grinding mills of various types, washing, jigging. classifying, tabling and possibly drying and sintering equipment, so arranged that with every change in the structure or analyses of the ore operating units can be cut in or out of the circuit. This sounds like an expensive plant to build and to operate, neither of which can be accepted at the present time. Gravity
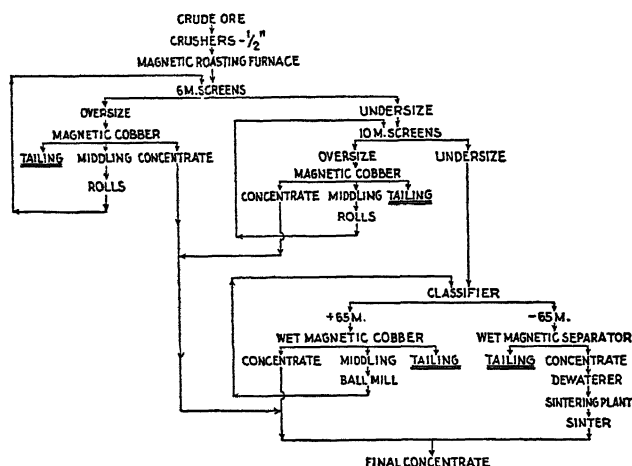
FIG. 1.—MAGNETIC ROASTING AND CONCENTRATION FLOW SHEET.

concentration, which is contemplated in the plant described above, is satisfactory with a uniform feed of uniform ore but does not readily accommodate radical and rapid fluctuations. The trend on the Mesabi Range is toward this type of plant but work has not proceeded beyond crushing, washing, screening and, to a very small degree, jigging. The general outgrowth of present developments is toward a plant equipped to wash and, when necessary, jig the ore. The next step will be to grind the middling or tailing and make the desired separation on tables or by some other process. Jigging is being tried extensively at a few plants and before long a considerable amount of jig concentrate undoubtedly will be produced annually. Tables were once used extensively on the Mesabi and these may come back into general use again. Other methods for treating fine ore are being considered and experimented with, such as the Rheolaveur process and the Fahrenwald classifier, and for the Cuyuna manganiferous ores, flotation. However, with a large proportion of the lean ores, these processes cannot succeed on account of the

small difference in weight between the hard dense silica and the soft porous partly leached iron oxide. For the taconites, they cannot be considered. It appears, therefore, that gravity concentrating processes are limited in their usefulness to ores of a definite structure and there is little indication that developments along this line will materially reduce the burden on the high-grade ore mines. With this understanding of the situation, it is interesting to consider what possible methods of concentration can be expected to reduce the demand on the high-grade ore mines. In this connection, magnetic concentration is receiving some consideration. By giving nearly any of the Mesabi lean ores, including the taconites, a magnetic roast and then using magnetic concentrating equipment, a high-iron low-silica concentrate can be produced. The flow sheet can be arranged so that good concentrate is recovered and low tailing rejected after each crushing step. By this means, a minimum of fine concentrate is produced, which requires sintering. The general flow sheet (Fig. 1) shows this plan of treatment.

MAGNETIC ROASTING FURNACE

In this flow sheet the only new and untried equipment is the magnetic roasting furnace. The roasting of hematite to magnetite is a very simple process. The ore should be heated to a dull red and then brought into a reducing atmosphere for a short time. The time required in the reducing atmosphere depends on the size and porosity of the particles and the intimacy of contact with the reducing gases. If all of the heat in the stack gases and in the ore discharged from the furnace were conserved, only about 23 lb. of coal would be required for the reduction of one long ton of ore. Actual calculations checked to a certain degree by laboratory work on a reasonably large scale indicate that about 160 lb. of coal or equivalent fuel will be required for roasting a long ton of ore assaying about 40 per cent. iron and 6 per cent. moisture. Much work has been done on the magnetic roasting of hematites,[1] but it remains for a plant of commercial size to demonstrate the actual cost of this operation. Many of the furnaces proposed have been of the rotary-kiln type but more satisfactory results were secured in the laboratory of the Mines Experi-

[1] W. B. Phillips: Notes on the Magnetization and Concentration of Iron Ore. *Trans.* A. I. M. E. (1895) **25**, 399–423.

Concentration by the Goltra Process. *Iron Age* (1914) **94**, 1148–1150.

J. Percy: Metallurgy. Iron and Steel, 17. London, 1864. J. Murray.

E. Clark, Jr.: Ore Dressing and Smelting at Pribram, Bohemia. *Trans.* A. I. M. E. (1880–1881) **9**, 420–461.

C. Jones.: The Magnetization of Iron Ore. *Trans.* A. I. M. E. (1890–1891) **19**, 289–296.

E. W. Davis: Magnetic Concentration of Iron Ore. Univ. Minn. School of Mines Experiment Station *Bull.* (1921) 9.

O. Lee, B. W. Gandrud and F. D. DeVaney: Magnetic Concentration of Iron Ores of Alabama. U. S. Bur. Mines *Bull.* (1927) 278.

ment Station of the University of Minnesota by using a small Herreshoff
furnace for this work.   Gas or oil fuel is forced into the bottom hearth
of this furnace and air is blown into the third hearth from the bottom.
The fuel burns on the third hearth and the products of combustion pass
upward, preheating and drying the descending ore.   The hot ore then
passes down through the two lower hearths, where it meets strong reduc-
ing conditions and is changed to magnetite.   The ore is discharged hot
from this furnace and must be cooled to below 100° C. before coming into
contact with air; otherwise it will burn back to hematite.   This ore when
properly roasted is strongly magnetic and can be concentrated in any
suitable magnetic concentrating equipment, the actual plant flow sheet
depending to some extent on the nature of the ore.

Cost of Magnetic Roasting

From a study of the detailed costs of roasting copper ore, it is possible
to arrive at a fairly accurate cost for the magnetic roasting of the hema-
tite.   This cost has been estimated at $0.50 per ton for large-scale
operations.   This contemplates using pulverized coal for the heating
operation and a small amount of fuel oil for the reduction.   This cost
includes all operating charges, repairs and depreciation and is possible
of reduction to $0.40 per ton, but this is probably the minimum.   Assum-
ing a 40 per cent. iron ore, a 63 per cent. iron concentrate and a 95 per
cent. iron recovery, it will be necessary to roast $1\frac{2}{3}$ tons of ore for the
product of 1 ton of concentrate.   This means a roasting cost of about
$0.83 per ton of concentrate.   Various tests of this nature have indicated
that about two-thirds of the ore can be recovered as coarse concentrate
and one-third as fines requiring sintering.   At $1 per ton for sintering,
the sintering cost for $\frac{1}{3}$ ton of concentrate is $0.33, which, added to the
roasting cost, gives a cost of $1.16 per ton of concentrate.   The cost of
crushing, screening, grinding, classifying and magnetic concentration
will be about $0.30 per ton of concentrate, which brings the total cost
of treatment to about $1.50 per ton of shipping product.   These
costs are not necessarily conservative but have been assembled from
known costs at existing plants and can probably be accomplished in a
plant producing 5000 tons or more of concentrate per day.   These costs
include all operating charges, repairs, maintenance, depreciation and
overhead.   It is evident that the total is about $0.50 per ton more than
the present market will stand and the price of iron ore must increase at
least $0.50 and probably $1 per ton before this method of treatment can
be considered.   However, this price advance will undoubtedly come
when the high-grade ores are further depleted.
    If the cost of magnetic concentration can be more definitely deter-
mined in a commercial plant, there will be little speculation as to the

ability of this magnetic roasting and concentration plant to make the estimated costs. There is a possibility of securing these costs without the necessity of erecting a complete magnetic concentration plant. It is probable that jigging as a primary plant or as an adjunct to washing plants will come into general use before long. In some cases, the jigs can be operated so as to remove a considerable proportion of the ore as a high-iron low-silica concentrate. The jig middling or tailing can then be roasted and concentrated magnetically in a plant that is a rather simple addition to the washing and jigging plant. With this installation, it will be necessary to roast, fine-grind and magnetically concentrate only a small proportion of the ore, and possibly sintering can be dispensed with if the proportion of fine concentrate is not too great. In all probability, the introduction of magnetic roasting to the Mesabi Range will come through some means of this kind and this may pave the way for the straight magnetic concentration plant that will be able to concentrate nearly all of the low-grade ore into high-iron low-silica furnace products.

Summarizing the situation, it is evident that the high-grade low-silica ores are being rapidly depleted and conservation measures must soon receive careful consideration. Concentration methods have not reduced the requirement for these ores and probably cannot do so without a material increase in the price of iron ore. Foreign ores will tend to keep the price of iron ore from increasing but until the price does increase the high-grade ores must carry the burden of the shipments and, conversely, it follows that as long as the high-grade ores can carry the burden of the shipments, the price will not increase.

DISCUSSION

R. H. SWEETSER, Columbus, Ohio.—This problem is similar to the one we had recently in Pittsburgh. The whole steel industry is based on a unit of iron and a unit of heat, and it looks as though the ore-dressing problem of enriching the iron ore has many phases similar to those in enriching coal. Those who visited the Champion plant were agreeably surprised to see the wonderful things they are doing in the recovering of the very fine coal, 100-mesh and 200-mesh material. They are faced with the problem of drying, and they are not only using filters and mixing the wet fines with the dry coarse coal, but they are also going to dry with heat and put their very fine coal through long dryers and use part of the slack coal for furnishing the heat.

As far as the blast-furnace man is concerned, the coal people are facing the same kind of problems that the ore people are facing in enriching their raw material.

It seems to me that there is a fine chance for some close teamwork. I think we are going to have engineers who are bright enough to work out the problems in enriching the ore. It has to be done at a low price. If it is not, there is no market for the low-grade ores.

The coal people discussed at their Pittsburgh meeting how much they ought to get for cleaning coal. One man made the statement that a coal man ought to get enough extra to pay for the cleaning of the coal. He is not entitled to any such thing. He is entitled to only the market value of his coal. If his coal is so dirty

that he can not put it on the market and get the full market price, he must stand the cost of the cleaning himself. It is the same with the iron-ore people. Those with low-grade ores will have to meet the competition of the high-grade ores.

So it seems to me that the blast-furnace men and the iron-ore people and the coal people are tied up together in a wonderful problem, and I think that the engineers are going to work it out.

R. O. HOCKING, Nashwauk, Minn.—It would seem to me that we need not concern ourselves very much regarding the future of the Lake Superior district. Considerable research work has been done during the past few years, and is now fairly intensive. I believe that the flow sheet that will be developed to treat the rougher wash-ore material will include jigging and tabling, to be followed possibly by magnetic concentration. The matter of magnetic concentration costs is very important and, as brought out by Mr. Davis, can be accurately determined in so far as concerns this district only by actual experience. We have produced around 2,000,000 tons of jigged concentrate during the past two years and the product has been of excellent quality and structure. Experiments made by us on tabling a sized feed are very encouraging and will undoubtedly lead to extensive treatment of material difficult to concentrate by any other means.

I think that there can be visualized tremendous possibilities. The Western Mesabi district—or that portion of the range lying between Keewatin and Grand Rapids—contains an immense tonnage of more or less rough material formerly classified as "indeterminate" and/or "no good." I am inclined to believe that considerable early drilling done from 1900 to 1910 was not properly supervised. Samples of many thousands of feet of drilling have been lost or thrown away, with the result that the only information available is the drill-runner's log—a not very satisfactory record. Considerable of this material noted as "taconite and ore" by the drill runner was not assayed, and, therefore, no analyses are available. We have found it necessary to reclassify thousands of feet of drill samples, and have recently found it possible to make a desirable product from some of the very rough material by crushing, washing and jigging. Ore reserves will be substantially increased, from time to time, by the wider use of such methods. A tremendous tonnage of rough material in the district can be beneficiated by the simple process of jigging and tabling.

Mr. Davis' point regarding the small difference in the specific gravity of the porous hematite and the dense silica is well taken. The presence of porous hematite in material fed to jigs affects the tonnage recovery materially, because a large proportion will go off with the dense gangue as a tailing. It is likely that the flow sheet best adapted to treat the rougher ores will contain jigs to produce the bulk of the total concentrate in coarse sizes, around 1 in., to be followed by recrushing and further treatment, probably tabling, to recover any values, especially the porous hematite, not recovered by the jigs. Tonnage recovery will thus be increased to the maximum amount, by wet methods. The final tailing from a flow sheet on the above lines would be amenable to magnetic concentration, provided sufficient values were contained therein.

This immense tonnage of lean, rough material on the Western Mesabi, supplemented by the lean ores on the Eastern Mesabi and the nonmerchantable ores on the Cuyuna Range, some of which are now being beneficiated by drying and sintering, and others to which are being applied processes more or less in the experimental stage, will prolong to a considerable degree the life of the Lake Superior district.

Resistance of Iron Ores to Decrepitation and Mechanical Work*

By T. L. Joseph† and E. P. Barrett,‡ Minneapolis, Minn.

The United States Bureau of Mines has been studying the blast-furnace process for about ten years. An experimental furnace was developed by the Bureau in cooperation with the Minnesota School of Mines Experiment Station, University of Minnesota. Many data have been obtained and published.[1] Royster, Joseph and Kinney§[48] found that the particle size of ore had an important effect upon the blast-furnace process. Kinney[28] stated:

> Economy in blast-furnace practice depends largely upon efficient gas-solid contact in the shaft of the furnace. If efficient work is not done in the shaft, the hearth and bosh will not function properly. A condition may be readily imagined where the particles of ore in the shaft are so large that the time entailed in the descent of these materials into the bosh is not sufficient to permit proper reduction and preparation prior to the time the ore enters the bosh of the furnace. Another condition may be pictured where the density of the stock column and the flow of stock is such that the ore will take one course and the gas another. Both of these examples will result in insufficient contact between the gas and the ore. Unreduced ore will reach the hearth, and the gas which has not been efficiently oxidized will reach the stock line. The result is the use of an excess of carbon in the smelting process.

It is obvious that fine ore particles occurring in the ore as charged, or formed in the furnace due to heat and mechanical action, place a definite limitation upon the efficiency of the operation. There is also an economic loss of fine material as dust.

Effect of Size of Material

Kinney reported (p. 83[29]) the reduction of iron oxides between planes at three furnaces as given in Table 1. The Chicago furnace was operated on Lake ores. Distribution of gas was not good and much of the charge passed into the hearth before the iron oxide was reduced. The Holt furnace was operated on coarse ore. Distribution of gas was fairly uni-

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TABLE 1.—*Comparison of Reduction between Planes at Three Furnaces*[29]

Plane	Distance Below Stock Line		Furnace					
			Ironton, Utah		Holt, Alabama		No. 4, South Chicago	
	Feet	Inch	Per Cent.	Cum. Per Cent.	Per Cent.	Cum. Per Cent.	Per Cent.	Cum. Per Cent.
1......................	3	0	20.2		18.9		4.2	
2......................	21	7	76.4	20.2	61.6	18.9	20.2	4.2
Top of bosh.............			3.4	96.6	19.5	80.5	75.6	24.4
Tuyere level.............				100.0		100.0		100.0

Distance from stock line to tuyeres, feet...62.58   60.33   68.083
Distance from tuyeres to point of observation near top
  of bosh, feet..........................19   19.25   24

form, and rapid reduction resulted. The Utah furnace was operated on the so-called layer filling method. Three sizes of ore were charged— coarse, medium and fine. Twice as much fine ore as coarse ore was available, so that the order of charging was as follows: coarse, fine, medium, fine, coarse, fine, medium, fine. The coarse ore passed a 3-in. screen and 95 per cent. remained on 1 in. All of the medium ore passed a 1½-in. screen and 79 per cent. remained on ¾ in. The fine ore passed a ¾-in. screen and 80 per cent. remained on ½ in. Each charge contained only one size of ore, with the necessary coke and limestone.

Table 2 gives the decrease in coke consumption and the increase in tonnage with each change in ore size.

TABLE 2.—*Cumulative Effect of Sized Ore on Furnace Operation*

Period	Ore Sizes	Coke, Lb. per Ton Iron		Iron, Tons per Day	
		Consumed	Reduction	Produced	Increase
		FOUNDRY IRON			
A	No sizing	2,713	0	280	0
B	2	2,402	311	337	87
D	3	2,225	488	360	110
		BASIC IRON			
A	No sizing	2,457	0	314	0
B	2	2,122	335	376	62
D	3	2,024	437	396	82

Joseph[16] proposed that an improvement in the gas-solid contact in blast furnaces operating on fine Mesabi ores might be made by screen-sizing the ores and sintering the finer portions. A large amount of the

potential flue dust would be eliminated. The decrease in the finer sizes and the increase in the coarser sizes should result in more even distribution of gas and increased coke efficiency.

POTENTIAL FLUE DUST

Table 3 shows that flue dust is composed largely of material finer than 14 mesh.

TABLE 3.—*Results of Screen-sizing Tests on Flue Dusts*

Screen Size	Per Cent. by Weight							
	Southern District[a]							Northern District[b] No. 8
	No. 1	No. 3	No. 5	No. 6	No. 4	No. 2	No. 7	
— 8 mesh..................	0.0	0.1	0.4	1.9	7.0	6.9	8.4	0.7
— 8 + 10 mesh...........	0.0	0.1	0.8	1.5	2.4	6.0	6.6	
— 10 + 14 mesh...........	0.0	0.3	1.5	1.9	2.8	6.9	8.0	1.2
— 14 + 28 mesh...........	0.0	5.3	14.3	12.8	13.0	27.4	28.1	6.3
— 28 + 35 mesh...........	0.5	10.2	13.4	14.1	12.2	15.5	14.4	
— 35 + 48 mesh...........	3.6	20.8	16.2	19.0	16.3	14.8	13.5	20.4
— 48 + 65 mesh...........	11.8	19.6	12.6	17.0	14.0	9.2	8.0	19.2
— 65 + 100 mesh...........	20.4	15.8	11.0	13.5	12.5	5.7	5.7	19.1
— 100 mesh................	63.7	27.8	29.8	18.3	19.8	7.6	7.3	33.1
Total....................	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] O. Lee, B. W. Gandrud and F. D. DeVaney: Magnetic Concentration of Flue Dust of the Birmingham District. U. S. Bur. Mines *Rept. of Investigations* No. 2761 (1926) 3.

[b] C. C. Furnas: Flow of Gases through Beds of Broken Solids. U. S. Bur. Mines *Bull.* 307 (1929) 94.

Furnas (p. 7[6]) states that in average blast-furnace practice all particles finer than 14 mesh may be considered as lifted by the gas stream. Furnas and Joseph[7] conducted a series of laboratory experiments with a gas stream that had approximately the same lifting power as the gas stream in a blast furnace. Their results are plotted in Fig. 1, which shows that the proportion of flue dust blown out increases progressively as the amount of fines in the bed increases. Two points from the operation of commercial furnaces are included in the graph and coincide well with the experimental points.

PURPOSE OF INVESTIGATION

The purpose of this investigation was to ascertain which ores would show the greatest decrease in size inside the blast furnace. The data obtained should be useful in selecting ores to be screened and sintered. Screen analyses on the natural ores do not give a true measure of their structure and relative resistance to decrepitation and mechanical work.

METHOD OF TESTING

In order that a definite amount of work might be applied to samples of iron ore while cold and while being heated to some definite temperature,

a small batch-type rotary kiln with internal firing was used (Fig. 2). The rate of heating was approximately that found by Kinney (Table 12[27] and Fig. 34[29]), from cold to 1400° F. in 1½ hr. The inside dimen-
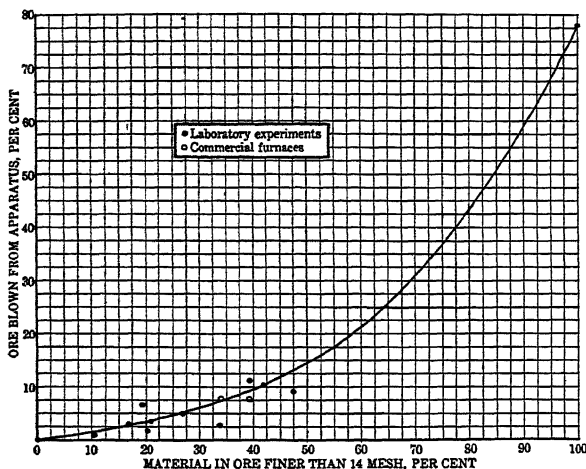
FIG. 1.—RELATION BETWEEN FINE MATERIAL IN CHARGE AND AMOUNT BLOWN OUT UNDER BLAST-FURNACE CONDITIONS.

sions are diameter 31 in., length 49 in. Samples of iron ore, about 300 lb. each, were air-dried and sampled for chemical analyses. Each lot was screened on a shaking screen. Material finer than 14 mesh was sampled and screened on a Ro-Tap machine. Two lots were prepared from the various screen-sized material, one for testing cold, the other for testing hot.
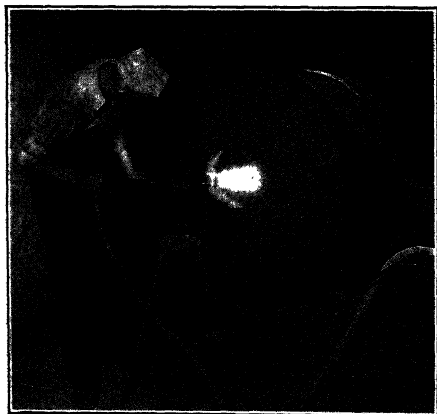
One lot was charged into the batch-type rotary kiln. After the kiln had been rotated for 1½ hr. the material was removed and screened. The change in the screen analysis of the ore as received and after having been rolled in the kiln for 1½ hr. was considered to have been due to mechanical work.

FIG. 2.—BATCH-TYPE ROTARY KILN.

The other lot of ore was charged into the kiln and heated to 1400° F. while being rolled for 1½ hr. The ore was cooled over night in the kiln, removed and screened. The change in the screen analysis of the ore as received and after having

been heated to 1400° F. while being rolled for 1½ hr. was considered to have been due to mechanical work plus heat.

ANALYSES OF ORES

The types of ore, the districts in which they occur and their analyses are given in Table 4.

TABLE 4.—*Type, District and Analysis of Ores Tested*

Number	Type	District	Analyses, Per Cent.				
			Fe	Mn	SiO₂	Al₂O₃	Loss on Ignition
1	Hematite	Mesabi	62.6	0.2	6.44	1.34	3.45
2	Hematite	Mesabi	44.7	1.7	32.38	0.96	2.39
3	Hematite	Mesabi	55.1	3.0	8.3	2.90	6.65
4	Limonitic manganiferous	Cuyuna	39.8	8.2	14.8	5.12	15.10
5	Hematite	Mesabi	64.7	0.3	2.64	0.88	3.75
6	Hematite	Mesabi	62.2	0.7	2.30	2.78	5.37
7	Hematite	Mesabi	56.8	1.4	6.42	1.74	8.60
8	Hematite	Cuyuna	62.5	0.2	5.04	5.58	2.06
9	Manganese	Imported	6.1	51.0	6.83	1.85	4.15
10	Hematite	Mesabi	60.0	1.9	5.04	3.68	2.76
11	Limonite	Mesabi	59.5	0.3	3.18	1.32	10.13
12	Hematite	Mesabi	61.3	4.2	1.84	1.13	3.70
13	Hematite	Mesabi	56.9	0.3	11.92	1.01	4.20
14	Hematite	Mesabi	55.8	0.6	9.74	3.47	5.80
15	Limonitic manganiferous	Cuyuna	48.7	6.3	3.24	4.52	13.42
16	Limonitic manganiferous	Cuyuna	46.0	5.32	6.84	4.64	13.42
17	Limonite	Marquette	51.0	0.3	15.38	0.74	7.70
18	Hematite	Marquette	54.5	0.8	15.15	3.05	1.49
19	Hematite	Western	58.0	0.2	9.98	3.71	2.02
20	Magnetite	Western	51.1	1.0	7.00	2.88	3.33
21	Hematite	Mesabi	48.7	4.5	8.18	8.07	12.04
22	Hematite	Southern	38.2	0.2	9.00	5.25	12.80
23	Hematite	Southern	37.8	0.4	14.37	4.81	12.52
24	Manganese	Imported	4.81	44.2	5.30	10.00	14.90
25	Hematite	Western	55.5	0.3	8.36	3.46	4.85
26	Hematite	Cuyuna	54.4	0.3	21.3	1.56	0.48
27	Hematite	Cuyuna	66.4	0.3	4.2	2.14	0.90
28	Manganese	Brazil	6.85	42.1	5.00	10.20	15.60
29	Manganese	Oriental	10.2	53.2	8.00	2.18	4.15
30	Manganese	Caucasian	2.4	46.3	7.78	2.36	11.06
31	Hematite	Vermilion	65.0	1.0	6.66	2.30	1.06
32	Hematite	Mesabi	48.0	0.3	6.7	5.22	12.15
33ᵃ	Hematite	Southern	36.6	0.6	14.1		18.35
34ᵇ	Hematite	Southern	34.8	0.4	20.9		8.65

ᵃ 20.8 per cent. CaO.
ᵇ 10.4 per cent. CaO.

TABLE 5.—*Changes in Average Particle Size Due to Cold and Hot Work Applied to Various Iron Ores*

Ore Number	Average Particle Size					
	As Received		After Cold Work		After Hot Work	
	Inches	Per Cent.	Inches	Per Cent.	Inches	Per Cent.
1	0.6621	100.0	0.5784	87.2	0.4142	62.3
2A	1.7080	100.0	1.4646	85.6	1.2376	72.4
2B	3.0	100.0			1.4157	47.2
2C	6.0	100.0			1.9293	32.2
3	0.5399	100.0	0.3859	72.9	0.3269	61.9
4	0.9116	100.0	0.5438	59.6	0.3204	35.2
5	0.1697	100.0	0.1410	82.9	0.1298	76.1
6	0.5248	100.0	0.3648	69.5	0.3267	62.4
7	0.3663	100.0	0.2978	81.4	0.2633	71.9
8	0.4115	100.0	0.3596	87.3	0.3658	88.9
9	5.2215	100.0	5.1868	99.3	3.2759	62.7
10	0.8658	100.0	0.4355	50.5	0.4084	47.2
11	1.0649	100.0	0.2124	19.5	0.1506	14.1
12	0.3579	100.0	0.3013	83.9	0.2660	70.2
13	0.4315	100.0	0.3504	81.1	0.3411	78.9
14	0.3395	100.0	0.2806	82.6	0.2215	65.2
15	0.2121	100.0	0.1824	86.0	0.1155	54.4
16	0.6355	100.0	0.4639	72.9	0.2353	37.0
17	1.1388	100.0	0.8875	78.2	0.6919	60.6
18	0.9958	100.0	0.9902	99.5	0.9382	94.2
19	0.9051	100.0	0.8257	91.3	0.8609	95.2
20	1.3167	100.0	1.1918	90.8	0.8614	60.5
21	0.2281	100.0	0.1910	83.6	0.1275	56.0
22	2.8872	100.0	2.3590	81.6	2.3390	80.6
23	1.6620	100.0	1.4050	84.4	1.2421	75.0
24	2.3148	100.0	2.0151	87.3	0.7059	30.4
25	0.7669	100.0	0.7141	93.0	0.6969	91.0
26	0.4610	100.0	0.3776	82.0	0.2460	53.4
27	0.5394	100.0	0.4215	78.2	0.4148	76.9
28	1.4480	100.0	1.2241	84.6	0.8771	60.6
29	1.9500	100.0	1.8638	95.5	1.0449	53.7
30	0.2413	100.0	0.2191	90.0	0.1240	51.5
31	0.2900	100.0	0.2449	84.5	0.2180	75.0
32	0.2003	100.0	0.1819	90.6	0.1376	68.6
33	3.4135	100.0	3.4135	100.0	1.7378	50.9
34	1.4388	100.0	1.3778	95.9	1.3714	95.5
Av.	1.2842	100.0	1.0530	82.0	0.7950	61.9

Results of Screen Sizing

The changes in average particle size due to cold and hot work are shown in Table 5 and Fig. 3. The average percentage change in average particle size was 18.0 per cent. due to cold work and 38.1 per cent. due to
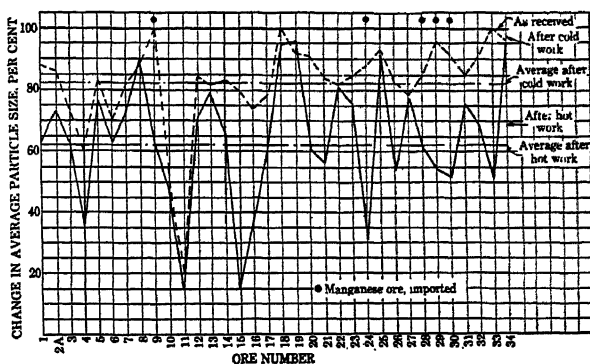
Fig. 3.—Ore-particle size after cold work and hot work compared with as-received condition.

hot work. The percentage changes shown in Fig. 3 have been grouped as shown in Table 6.

Table 6.—*Average Percentage Change in Average Particle Size*

Change in Average Particle Size, Per Cent.	Number of Samples	
	After Cold Work	After Hot Work
0	3	0
1 to 5	2	2
5 to 10	5	2
10 to 15	4	1
15 to 20	11	1
20 to 25	3	5
25 to 30	2	3
30 to 50	3	14
Over 50	1	6

Material Finer than 14 Mesh

The percentage of material finer than 14 mesh as received, both after cold work and after hot work, is shown in Fig. 4. These percentages have been grouped as shown in Table 7.
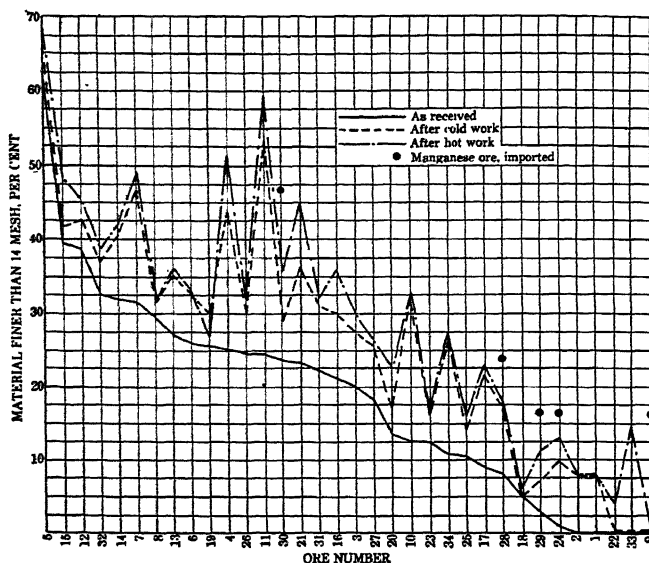
FIG. 4.—ORE FINER THAN 14 MESH AFTER COLD WORK AND HOT WORK COMPARED WITH AS-RECEIVED CONDITION.

TABLE 7.—*Percentages of Material Finer than 14 Mesh Grouped*

Material Finer than 14 Mesh, Per Cent.	Number of Ores		
	As Received	After Cold Work	After Hot Work
0 to 1	6	3	1
1 to 5	2	1	1
5 to 10	2	4	3
10 to 15	5	1	3
15 to 20	2	3	3
20 to 30	11	8	6
30 to 40	5	6	9
40 to 50	0	6	5
Over 50	1	2	3

TESTS ON MANGANESE ORES

Five imported manganese ores were tested in the same manner as were the iron ores. These were numbered 9, 24, 28, 29 and 30. The curves in Fig. 3 show that all of these ores were little affected by cold work, but much altered by hot work. Only one of the samples contained more than 20 per cent. material finer than 14 mesh. One of the samples after hot work contained no material finer than 6 mesh.

STACK LOSS OF MANGANESE IN FERRO FURNACES

Clements (p. 351[3]) gives the analyses of light dust from stoves and chimneys as shown in Table 8.

TABLE 8.—*Analysis of Light Dust from Stoves and Chimneys.*[3]

	Light Dust from Chimney Foot, Per Cent.	Light Dust from Hot-blast Stove, Per Cent.
SiO$_2$	14.90	14.90
Fe$_2$O$_3$	1.64	1.00
Al$_2$O$_3$	10.38	8.54
MnO	20.07	17.94
CaO	13.10	12.30
MgO	0.60	0.95
BaSO$_4$	1.90	1.70
K$_2$O	13.78	13.00
Na$_2$O	0.86	0.74
SO$_3$ (soluble)	16.88	14.10
P$_2$O$_5$	0.201	0.164
Loss on ignition	3.10	Not given

In view of the much higher concentration of manganous oxide in the charge as compared to that of alumina, silica and lime, it does not seem that manganese lost in the stack should be attributed to volatilization any more than the loss of alumina, silica and lime should be called volatilization. The large amount of coke compared to ore has a much greater abrasive effect upon the ore in the ferro furnace. In a pig-iron furnace the weight of the ore is twice that of the coke; that is, 4000 lb. of ore and 1800 lb. of coke. In a ferro furnace the weight of the coke is greater than that of the ore; that is, 4500 to 5000 lb. of coke and 4000 lb. of ore.

Decrepitation tests on manganese ores indicate that they may break down a great deal when heated and subjected to the abrasive action of the coke in the blast-furnace stack. It may be that the finely divided oxide of manganese is not collected in the chimney and stoves; therefore the analyses given by Clements do not give the true proportion of manganous oxide, alumina, silica and lime lost as dust. However, the high percentage of potassium oxide in the dust samples indicates that much very fine dust is caught in the stoves and chimneys.

TESTS ON LIMESTONE

Three samples of limestone were tested in the same manner, as were the iron ores. The samples were all in large lumps and were broken to a small extent only. The screen analyses of the three samples, as received, after cold work and after hot work are given in Table 9.

TABLE 9.—*Screen Analyses of Three Limestones*

Screen Size Mesh	As Received		After Cold Work		After Hot Work	
	Per Cent.	Cumulative Per Cent.	Per Cent.	Cumulative Per Cent.	Per Cent.	Cumulative Per Cent.
Blue limestone						
−6 + 4	55.0	55.0	51.3	51.3	49.0	49.0
−4 + 2	45.0	100.0	40.9	92.2	41.6	90.6
−2 + 1			7.8	100.0	9.4	100.0
White limestone						
−6 + 4	43.7	43.7	43.0	43.0	42.4	42.4
−4 + 2	56.3	100.0	57.0	100.0	57.0	99.4
−1.05					0.6	100.0
Brown limestone						
−6 + 4	62.5	62.5	58.6	58.6	50.6	50.6
−4 + 2	37.5	100.0	40.0	98.6	37.1	87.7
−2 + 1.05			1.4	100.0	3.6	91.3
−0.525					8.7	100.0

CONCLUSIONS

The following conclusions may be drawn from the results of this investigation:

1. Screen analysis of an ore does not indicate its behavior when subjected to abrasion and heat.

2. Average decrease in average particle size was 18.0 per cent. due to cold work and 38.1 per cent. due to hot work.

3. These tests indicate the relative amount of potential flue dust that might be produced from each of the ores.

4. A method was developed which might be used in selecting ores for mixing in a blast furnace in order to obtain better gas-solid contact in the stack.

5. This method of testing ores should be of value in selecting ores for screening and sintering of the finer sizes.

6. Imported manganese ores are little affected by cold work but much changed by hot work.

7. Limestone is very resistant to cold work and to hot work at a temperature of 1400° F.

SELECTED BIBLIOGRAPHY

1. J. F. BARKLEY: Blast-furnace Gas Studies. U. S. Bur. Mines *Tech. Paper* 401 (1927) 9 pp.

2. A. W. BELDEN: Metallurgical Coke. U. S. Bur. Mines *Tech. Paper* 50 (1912). 48 pp.

3. F. CLEMENTS: Blast-furnace Practice, **3**. London, 1929. Benn.

4. A. L. FEILD: A Method for Measuring the Viscosity of Blast-furnace Slag at High Temperatures. U. S. Bur. Mines *Tech. Paper* 157 (1916). 29 pp.

5. A. L. FEILD and P. H. ROYSTER: Slag Viscosity Tables for Blast-furnace Work. U. S. Bur. Mines *Tech. Paper* 187 (1918). 38 pp.

6. C. C. FURNAS: Flow of Gases Through Beds of Broken Solids. U. S. Bur. Mines *Rept. of Investigations* No. 2904 (1928).

7. C. C. FURNAS and T. L. JOSEPH: Blast-furnace Filling and Size Segregation. *Trans.* A. I. M. E., Iron and Steel Div. (1929) 98–124.

8. T. L. JOSEPH: Combustibility of Coke and Rate of Combustion. U. S. Bur Mines *Rept. of Investigations* No. 2604 (1924). 5 pp.

9. T. L. JOSEPH: Effect of Sulfur on the Blast-furnace Process: *Trans.* A. I. M. E. (1925) **71**, 453–473; discussion, 473–475.

10. T. L. JOSEPH, P. H. ROYSTER and S. P. KINNEY: Effect of the Physical Properties of Ore and Coke on the Capacity of the Blast Furnace. *Proc.* Engrs. Soc. of Western Pennsylvania (1925) **41**, 428–446.

11. T. L. JOSEPH, P. H. ROYSTER and S. P. KINNEY: Utilization of Manganiferous Iron Ores: U. S. Bur. Mines *Tech. Paper* 393 (1926). 28 pp.

12. T. L. JOSEPH and S. P. KINNEY: Minnesota Manganiferous Iron Ores in Relation to the Iron and Steel Industry: School of Mines Expt. Sta., Univ. of Minnesota *Bull.* 12 (1927). 101 pp.

13. T. L. JOSEPH, E. P. BARRETT and C. E. WOOD: Minnesota Manganiferous Iron Ores in Relation to the Iron and Steel Industry: *Trans.* A. I. M. E. (1927) **75**, 292–337; discussion, 338–345.

14. T. L. JOSEPH, S. P. KINNEY and C. E. WOOD: Production of High-alumina Slags in the Blast Furnace: U. S. Bur. Mines *Tech. Paper* 425 (1928) 32 pp.; also, Iron and Steel Technology, A. I. M. E. (1928) 66–85.

15. S. P. KINNEY: Combustion of Coke at the Tuyere Level of the Blast Furnace. *Blast Furnace and Steel Plant* (1925) **13**, 243–247.

16. T. L. JOSEPH: Importance of Gas-solid Contact in the Blast Furnace. *Fuels and Furnaces* (1928) **6**, 635–640.

17. S. P. KINNEY: Furnace Lining Wears Unevenly. *Iron Age* (1925) **115**, 1639–1640; discussion by W. Mathesius, H. E. McDonnel and A. Farrell, 1848–1849.

18. S. P. KINNEY: Iron Hottest at Middle of Cast: *Iron Age* (1925) **116**, 466–467.

19. S. P. KINNEY: Material and Heat Balance of a Southern Foundry Furnace. *Blast Furnace and Steel Plant* (1925) **13**, 272–276.

20. S. P. KINNEY and E. W. GUERNSEY: The Occurrence of Alkali Cyanides in the Iron Blast Furnace. *Ind. & Eng. Chem.* (1925) **17**, 670–674. Reprint in *Blast Furnace and Steel Plant* (1925) **13**, 395–399.

21. S. P. KINNEY and F. B. McKENZIE: Proposed Change in Blast-furnace Design. *Iron Age* (1925) **115**, 476–478; discussion, 707. Reprint in *Iron and Coal Tr. Rev.* (1925) **110**, 429.

22. S. P. KINNEY: Composition of Materials from Various Elevations in an Iron Blast Furnace. U. S. Bur. Mines *Tech. Paper* 397 (1926). 21 pp.

23. S. P. KINNEY and E. W. GUERNSEY: Occurrence, Distribution and Significance of Alkali Cyanides in the Iron Blast Furnace. U. S. Bur. Mines *Tech. Paper* 390 (1926). 37 pp.

24. S. P. KINNEY, P. H. ROYSTER and T. L. JOSEPH: Study of the Reactions in an Iron Blast Furnace. U. S. Bur. Mines *Rept. of Investigations* No. 2747 (1926). 11 pp.

25. S. P. KINNEY: Relation of Carbon Consumption to Material Smelted in the Blast Furnace. *Blast Furnace and Steel Plant* (1926) **14**, 15.

26. S. P. KINNEY: Iron Blast-furnace Reactions. U. S. Bur. Mines *Tech. Paper* 391 (1927). 65 pp.
27. S. P. KINNEY: The Blast-furnace Stock Column. U. S. Bur. Mines *Tech. Paper* 442 (1929). 148 pp.
28. S. P. KINNEY: Ore Size and Blast-furnace Economy. U. S. Bur. Mines *Rept. of Investigations* No. 2983 (1930).
29. S. P. KINNEY: Effect of Sized Ore on Blast-furnace Operation. U. S. Bur. Mines *Tech. Paper* 459 (1930). 92 pp.
30. O. LEE, B. W. GANDRUD and F. D. DEVANEY: Magnetic Concentration of Flue Dust from Blast Furnaces in the Birmingham District. U. S. Bur. Mines *Rept. of Investigations* No. 2761 (1926). 16 pp.
31. G. ST. J. PERROTT and S. P. KINNEY: Shatter and Tumbler Test for Metallurgical Coke. *Ind. & Eng. Chem.* (1922) **14**, 926–941.
32. G. ST. J. PERROTT: Properties of Metallurgical Coke. *Proc.* Amer. Soc. Test. Mat. (1923) **23**, 475–493; discussion, 450–500.
33. G. ST. J. PERROTT and S. P. KINNEY: Combustion of Coke in the Blast-furnace. *Trans.* A. I. M. E. (1923) **69**, 543–584.
34. A. R. POWELL and J. H. THOMPSON: Study of Desulphurization of Coke by Steam. Carnegie Inst. of Tech. *Bull.* 7 (1921). 50 pp.
35. A. R. POWELL: Forms of Sulfur in Coke, and Their Relations to Blast-furnace Reactions. *Trans.* A. I. M. E. (1923) **69**, 587–599; discussion, 599–605.
36. T. T. READ, T. L. JOSEPH and P. H. ROYSTER: Effect of Silica in Iron Ore on Cost of Pig-iron Production. U. S. Bur. Mines *Rept. of Investigations* No. 2560 (1924). 10 pp. Reprint in *Iron Tr. Rev.*, 1924 **74**, pp. 288–291.
37. T. T. READ: Raw Materials Affect Pig-iron Costs. *Iron Tr. Rev.* (1924) **74**, 1424–1425; *Iron Age* (1924) **113**, 1698–1699.
38. T. T. READ: Probable Error in Blast-furnace Records and Calculations Therefrom. *Trans.* A. I. M. E. (1926) **73**, 1009–1025.
39. T. T. READ: General Principles of Beneficiation of Iron Ores. *Blast Furnace and Steel Plant* (1926) **14**, 172–179; 265–273; 294–297; 350–356.
40. P. H. ROYSTER and T. L. JOSEPH: Pyrometry in Blast-furnace Work. Pyrometry, A. I. M. E. (1920) 544–566.
41. P. H. ROYSTER, T. L. JOSEPH and S. P. KINNEY: Progress in Blast-furnace Research. U. S. Bur. Mines *Rept. of Investigations* No. 2524 (1923). 6 pp.
42. P. H. ROYSTER and T. L. JOSEPH: Effect of Coke Combustibility on Stock Descent in Blast Furnaces. *Trans.* A. I. M. E. (1924) **70**, 224–232.
43. P. H. ROYSTER and T. L. JOSEPH: Study of Stock Flow in Furnaces. *Iron Tr. Rev.* (1924) **74**, 738–740.
44. P. H. ROYSTER, T. L. JOSEPH and S. P. KINNEY: Reduction of Iron in the Blast Furnace. *Blast Furnace and Steel Plant* (1924) **12**, 35–37.
45. P. H. ROYSTER, T. L. JOSEPH and S. P. KINNEY: Significance of Hearth Temperatures. *Blast Furnace and Steel Plant* (1924) **12**, 154–158.
46. P. H. ROYSTER, T. L. JOSEPH and S. P. KINNEY: Heat Balance of Bureau of Mines Experimental Blast Furnace. *Blast Furnace and Steel Plant* (1924) **12**, 200–204.
47. P. H. ROYSTER, T. L. JOSEPH and S. P. KINNEY: Time Element in Iron-ore Reduction. *Blast Furnace and Steel Plant* (1924) **12**, 246–250.
48. P. H. ROYSTER, T. L. JOSEPH and S. P. KINNEY: Influence of Ore Size on Reduction. *Blast Furnace and Steel Plant* (1924) **12**, 274–280.
49. R. A. SHERMAN and S. P. KINNEY: Combustibility of Blast-furnace Coke. *Iron Age* (1923) **111**, 1839–1844.
50. F. H. WILLCOX: Asphyxiation from Blast-furnace Gas. U. S. Bur. Mines *Tech. Paper* 106 (1916). 69 pp.

51. F. H. Willcox: Safe Practice at Blast Furnaces—a Manual for Foremen and Men.   U. S. Bur. Mines *Tech. Paper* 136 (1916).   73 pp.
52. F. H. Willcox: Blast-furnace Break-outs, Explosions, and Slips, and Methods of Prevention.   U. S. Bur. Mines *Bull.* 130 (1917).   280 pp.
53. F. H. Willcox: Occupational Hazards and Accident Prevention at Blast-furnace Plants, Based on Records of Accidents at Blast Furnaces in Pennsylvania in 1915.   U. S. Bur. Mines *Bull.* 140 (1917).   155 pp

Experiments Demonstrate Method of Producing Artificial Manganese Ore*

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Large deposits of manganiferous iron ores, representing several million tons of metallic manganese, occur in the United States. The Minnesota deposits of such ore are of outstanding importance because of their size, state of development, ease of mining and proximity to the Great Lakes, which permits water transportation to steel centers. In view of the fact that our steel industry requires large quantities of manganese, for which no satisfactory substitute has been found, and because our reserves of ferro-grade ore are comparatively small, the development of methods that will make our large deposits of manganiferous iron ores available as a source of ferromanganese is an important problem. Realizing the importance of this problem, some years ago the North Central Station of the U. S. Bureau of Mines and the Minnesota School of Mines Experiment Station undertook jointly the development of methods for recovering the manganese content of manganiferous iron ores in a form suitable for the production of ferromanganese, the 80 per cent. alloy indispensable in producing steel.

Two types of manganiferous iron ores have been described in previous reports.[1] The brown ores are higher in iron and lower in manganese than the black ores; the black ores are more siliceous but contain less phosphorus. The utilization of the iron content of the brown ores in the production of steel appears to furnish the best basis for their treatment. The method of attack has been to work out modifications in iron and steel practice so as to recover manganese in the form of slag comparable to ferro-grade ores.

The greater part of the experimental work has been conducted with a 6-ton blast furnace and a ½-ton basic open hearth. This paper is devoted mainly to open-hearth tests in which high-phosphorus spiegel

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[1] T. L. Joseph, and S. P. Kinney: Minnesota Manganiferous Iron Ores in Relation to the Iron and Steel Industry. *Trans.* A. I. M. E. (1927) **75**, 292; also *Bull.* 12, Univ. of Minn. School of Mines Expt. Station.

(12 to 15 per cent. Mn, 0.5 per cent. P) was treated to separate the manganese from the phosphorus and the iron. Only a portion of the data can be presented at this time; the complete results will appear later in a U. S. Bureau of Mines bulletin. Results from a series of electric-furnace heats are given to show that the high-phosphorus spiegel, produced from Cuyuna manganiferous iron ores, can also be treated in the electric furnace. These results make it possible to compare the operation when carried out in the open-hearth and in the electric furnace.

PRESENT USE OF MANGANIFEROUS IRON ORES

Several years of practice have shown that definite advantages accrue from the use of manganiferous iron ores and high-manganese pig iron. These advantages to blast-furnace practice, open-hearth practice, and in the finishing mills have been outlined in another paper.[2] In present practice, sufficient manganiferous iron·ore is added to the iron-ore mixture of basic blast furnaces to produce pig iron containing 1.5 to 2.0 per cent. manganese. The major portion of this manganese enters the open-hearth slag. The amount recovered in the steel depends upon open-hearth practice. Under favorable conditions, with a low slag volume and no run-off slag, about 30 per cent. of the manganese in the pig iron can be recovered as residual manganese—manganese in the steel at the end of the heat. With a loss of 25 per cent. in the blast furnace, about 20 per cent. of the manganese in the ore reaches the ingot. Under less favorable conditions involving large slag volumes and a run-off slag, practically all of the manganese passes into the slag. Data are not available to show the average prevailing conditions. A comparison over a 15-year period of the tons of manganese used in the form of manganiferous iron ores and the amount of manganese required to make a ton of steel indicates that the residual manganese resulting from the use of high-manganese pig iron has not materially decreased the amount of manganese required in the form of ferro and spiegel. A former report[3] by the authors shows that the amount of metallic manganese needed in the form of ferro and spiegel has not decreased in the past 15 years, although the amount of manganese derived from manganiferous iron ores has increased about tenfold. For example, in 1911 shipments of manganiferous iron ores contained 14,629 tons of metallic manganese. About 14 lb. of manganese were required per ton of steel that year. In 1927, the manganese content of manganiferous iron ores amounted to 153,756 tons, but 14.3 lb. of

[2] T. L. Joseph and S. P. Kinney: *Op. cit.*, 314–19.

[3] T. L. Joseph, E. P. Barrett and C. E. Wood: Production of Ferromanganese from Minnesota Manganiferous Iron Ores. *Proc.* First Annual Convention American Manganese Producers Assn. (1928) 49; also *Eng. & Min. Jnl.* (1929) **128**, 310.

manganese were still required to make a ton of steel. Although the manganese supplied in manganiferous iron ores is about one-half the total requirements in the form of ferro and spiegel, our needs for manganese in the form of these alloys have not decreased.

MANGANESE SPECIFICATIONS IN STEEL HAVE INCREASED

The manganese content of some new types of steel has increased markedly and general specifications have also increased. It appears that the residual manganese, made possible by the increased use of manganiferous iron ores, has approximately offset the amount of manganese needed to meet higher manganese specifications. If this were not true, one would expect an increase in the amount of manganese required per ton of steel during the last few years. It would require a survey of present blast-furnace and basic open-hearth practice to determine what final disposition is made of approximately 150,000 tons of metallic manganese supplied annually in manganiferous iron ores. Such a survey would show to what extent manganese in pig iron can properly be substituted for ferro and spiegel additions. It would be desirable to know whether greater amounts of residual manganese can be recovered without interfering with practice.

PRESENT PRACTICE AND PROPOSED MODIFICATIONS

Under present practice, sufficient manganiferous iron ore is added to the ore mixtures of blast furnaces making basic iron to produce metal containing from 1.5 to about 2.0 per cent. manganese (see flow sheet). When this high-manganese pig iron is charged into the basic open-hearth furnace with about equal or slightly greater amounts of steel scrap, most of the manganese passes into the slag, which will contain from 5 to 10 per cent. MnO. In the proposed practice to recover manganese in a form suitable for making ferro, manganiferous iron ores are not mixed with straight iron ore but make up the entire ore charge. In this procedure, high-phosphorus spiegel containing from 10 to 15 per cent. manganese is produced in place of basic pig iron with 1.5 to 2.0 per cent. manganese. By giving this spiegel a preliminary treatment, the manganese can be concentrated so that a slag containing from 55 to 70 per cent. manganous oxide will be produced in place of normal open-hearth slag containing from 5 to 10 per cent. manganous oxide. The basic idea underlying the proposed practice is to concentrate the manganese to a point where a product suitable for making ferro will be produced. In present practice the manganese is diluted with lime, silica and alumina, and contaminated with phosphorus to such an extent as to limit its use in making high-manganese pig iron and prohibit its use for making ferromanganese or spiegel. In normal open-hearth slags, lime, iron oxide and

silica are the principal constituents.   However, when an alloy containing 15 per cent. Mn is oxidized by the usual open-hearth procedure of adding iron ore, and no limestone or dolomite is used, manganous oxide and ferrous oxide become the principal slag constituents.[4]   By adjusting the iron and phosphorus content, described in detail under open-hearth tests, an artificial ferro-grade product is produced.

BLAST-FURNACE TESTS

Industrial blast furnaces have never been operated on an ore charge made up entirely of brown manganiferous iron ores from the Cuyuna Range.   It was not known, therefore, whether a charge of 100 per cent. brown ore could be smelted without difficulty.   To test the behavior of such a charge and also to provide metal for small-scale open-hearth tests, a 6-ton experimental blast furnace was developed.   During a campaign of 6 weeks, about 150 tons of metal containing approximately 12 per cent.

Flow Sheet for Making High-manganese Pig Iron

Ore Mixture

5 per cent. manganiferous iron ore
95 per cent. iron ore

↓

Blast furnace

↓   ↓

High Mn pig iron   Slag
1.5 to 2.0
per cent. Mn

↓

Basic open hearth

↓   ↓

Steel   Slag
             5 to 10
             per cent.
             MnO
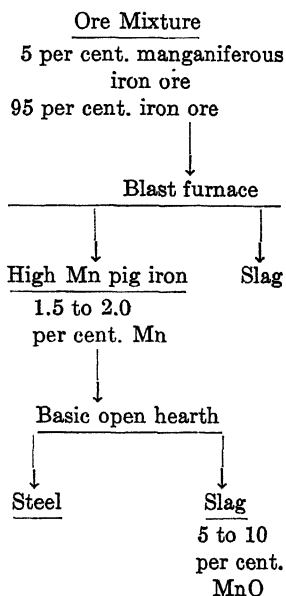
Flow Sheet for Making Ferromanganese from Manganiferous Iron Ores

PROPOSED PRACTICE

Ore Mixture

100 per cent. manganiferous iron ores

↓

Blast furnace

↓   ↓

High-phosphorus spiegel   Slag
12–15 per cent. Mn
4.5 per cent. C
0.5 per cent. P

↓

Preliminary basic open hearth to slag off Mn

↓   ↓

Metal   Slag containing
3.4 per cent. C   55–75 per cent. MnO
0.75 per cent. Mn
0.45 per cent. P
0.002 per cent. S
0.011 per cent. Si

↓   ↓

Basic open hearth   Blast furnace

↓   ↓   ↓   ↓

Slag   Steel   Ferromanganese Slag

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[4] High-manganese slags tend to build up the bottom rather than cut it down, hence very little lining or bottom is picked up.

Mn, 4.5 per cent. C, 0.25 per cent. Si, and 0.55 per cent. P were produced. A description of the furnace and a detailed report of its operation have been published.[5]

DESCRIPTION OF EXPERIMENTAL OPEN-HEARTH FURNACES

Experimental furnaces for studying the reactions of high-temperature processes do not closely duplicate all the conditions in industrial furnaces, but they have an advantage over laboratory studies pertaining to specific reactions in that all the physical and chemical forces are brought into play and an over-all or integrated result is obtained. It is not an easy matter to determine the scale upon which to make experimental furnaces so as to duplicate approximately full-size furnace conditions and to keep the cost of operation within the limits usually set for experimental work. The first open hearth used in connection with this problem held about 200 lb. of metal. It was a stationary furnace,[6] and was an economical piece of equipment for making a study of suitable refractories for working with high-manganese slags and arriving at a method for working the heats. When these preliminary investigations had been completed, a larger furnace of the tilting type was constructed.

A photograph of the open-hearth furnace used in making the heats described in this paper is shown in Fig. 1. Fig. 2 contains a drawing which shows a plan view and two elevations. The furnace proper consisted of a cylindrical shell, 8 ft. long and 4 ft. 8 in. dia., lined with refractories as shown in Fig. 2. The bottom and side walls were lined with magnesia with a chrome partition between the silica roof and the magnesite side walls. In order to facilitate the lining of the furnace, an opening slightly larger than the dimensions of the roof was provided in the top of the steel shell. This feature worked out very satisfactorily.

Underground checkers of standard soap brick were arranged as shown in Fig. 2. When the furnace was first fired, a bath temperature of 1600° C. could not be attained readily, presumably because of the distance from the underground checkers to the furnace proper and the drop in temperature of both the waste gases and the preheated air. When the uptakes were enlarged so that they could be filled with checkers, a temperature of 1600° C. was readily attained. The furnace was fired with oil burners designed by one of the authors and described by him in another report.[7] An exhauster, operating at a capacity of about 1600 cu. ft. of gas per minute, was used in preference to a chimney. This arrangement was satisfactory except for the fact that the distance traversed by the gases, moving through the vertical steel pipe shown in

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[5] T. L. Joseph and S. P. Kinney: *Op. cit.*

[6] T. L. Joseph and S. P. Kinney: *Op. cit.*, 325–327.

[7] E. P. Barrett: Simple, Efficient Oil Burner Constructed from Pipe Fittings. In press.

Fig. 1, was not long enough to cool the flue gases sufficiently before entering the exhauster. A fine spray of water injected into the steel pipe at its base overcame this difficulty. About 8 gal. of fuel oil were used per hour. The normal metal charge consisted of 500 lb. of spiegel. Charges of 1000 lb. were used, but 500 lb. was a convenient size of charge
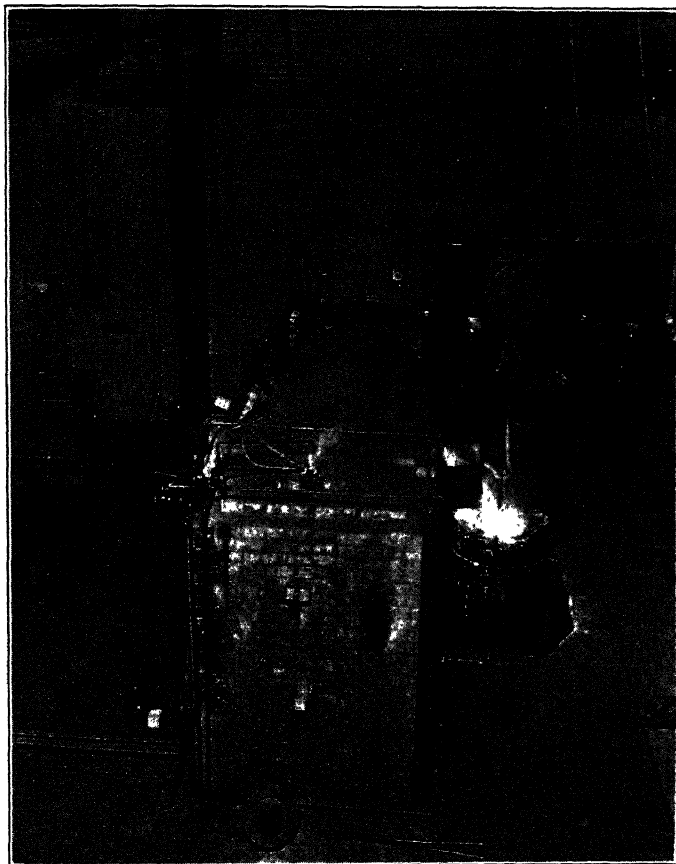
FIG. 1.—EXPERIMENTAL OPEN-HEARTH FURNACE.

and made it possible to get a greater number of heats from the same quantity of spiegel.

OPEN-HEARTH TESTS

In normal open-hearth practice the slag is the vehicle for carrying on the process. Slag composition and its physical properties are therefore important factors in open-hearth practice. The control and adjustment of the slag is, however, a means to an end—the production of good steel. In the preliminary open-hearth operation about to be described,

the production of slag that will meet the requirements of ferro-grade ore is the objective. The metal from this preliminary operation must be treated in another open-hearth furnace in order to produce steel. The manganese content of slag suitable for producing ferromanganese must be high, the ratio of manganese to iron must be about 9, the silica should be low, and the phosphorus should be 0.2 per cent. or under. A separation of the manganese in high-phosphorus spiegel from the iron and phosphorus must be made in order to meet these requirements. Manganese and phosphorus are oxidized by iron oxide at too nearly the same rate to effect a separation by oxidation. However, there is sufficient differential in the rates of reduction of phosphorus compounds, iron oxides, and manganese oxides to effect a separation. The method for doing this can be explained best by following the log of an individual heat and noting the changes in slag and metal composition as the heat progresses.

METHOD OF WORKING OPEN-HEARTH HEATS

If the proposed method of producing ferromanganese from manganiferous iron ores were carried out in actual practice, molten spiegel directly from a blast furnace or from a mixer would be charged into the open hearth and iron ore added immediately. Cold spiegel was charged into the open hearth in these experiments. Table 1 and Fig. 3 show that in heat 405 it required $1\frac{1}{2}$ hr. to melt the charge of cold spiegel. As soon
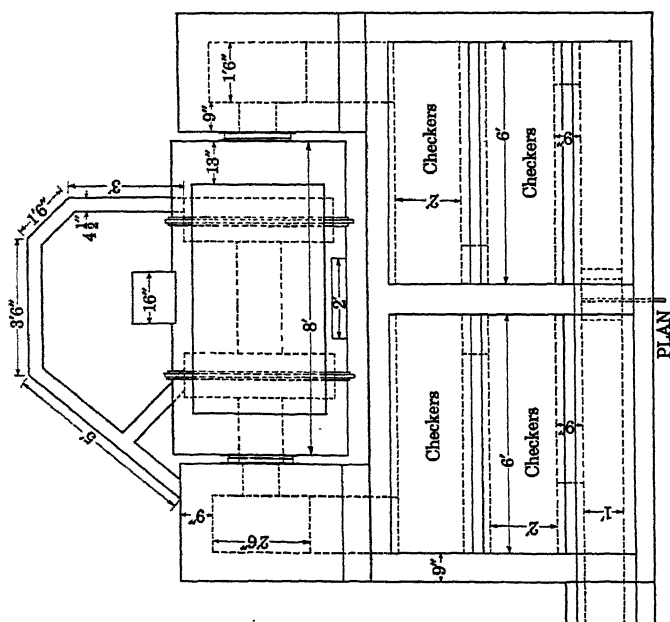
FIG. 2a.—CAPTION ON NEXT PAGE.
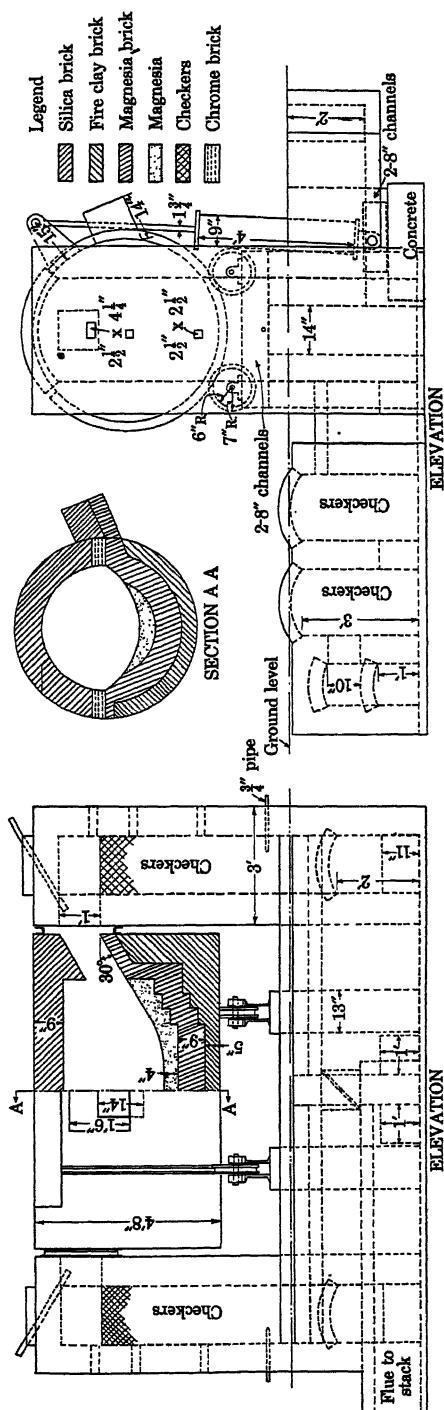
FIG. 2.—PLAN AND ELEVATION OF EXPERIMENTAL OPEN-HEARTH FURNACE.

as the charge was completely melted, 125 lb. of manganiferous iron ore was added. Hard hematite was generally ueed, but roll scale, manganiferous iron ore, and siliceous hematite were also used.

In heat 405 the manganese in the metal was 0.5 per cent., 1½ hr. after ore was added. At this time the slag contained 46.8 per cent. MnO, 34.4 per cent. FeO, and 8.8 per cent. insoluble. As a result of the low temperature, the phosphorus in the slag and the carbon in the metal were unusually high for this stage of the heat. The objective thus far was to oxidize the manganese. When the manganese in the metal was sufficiently low, as judged by the metal fracture—an uncertain method—the slag was covered with a layer of coke several inches thick. Coke breeze, usually available in steel plants, would be satisfactory for this purpose. In ½ hr. after the coke was added the phosphorus in the slag decreased from 1.86 to 0.95 per cent. and the FeO from 34.4 to 11.6 per cent. At this time the manganese in the metal was 0.3 per cent. The MnO in the slag increased from 46.8 to 61.5 per cent. as a result of the decrease in FeO from 34.4 to 11.6 per cent. Fig. 3 shows the changes in the composition of the slag and metal when the bath

was held under a coke layer. After 2.5 hr. the FeO in the slag had decreased to 4.7 per cent. and the phosphorus to 0.15 per cent. The phosphorus and carbon in the metal were approximately the same at the end of the heat as at the beginning. As the FeO decreased from 45.6 to 4.7 per cent. and the phosphorus from 1.86 to 0.15 per cent., the manganese in the metal increased 0.5 to 1.2 per cent.

The production of a slag from which ferromanganese can be made hinges upon the much faster rates at which FeO and the compounds of phosphorus can be reduced as compared to MnO.

The curves in Figs. 4 to 9, inclusive, show the same general characteristics as the curves for heat 405. The manganese in the spiegel charged varied from 5.3 per cent. in heat 418 to 17.3 per cent. in heat 242. Except for a better grade of slag and for a larger amount of slag when the manganese in the metal was higher, all the heats are much alike.

TABLE 1.—*Changes in Composition of Slag and Metal in Open-hearth Heats*

Hours after Charging	Metal, Per Cent.			Slag, Per Cent.				Temperature °C.
	Mn	P	C	MnO	P	FeO	Insoluble	
				Heat 405				
0	9.8	0.56	4.50					
1¼	7.6	0.55						1525
Ore added								
2	3.8	0.48		35.1	1.29	45.6	8.8	1525
2¾	0.5	0.18		46.8	1.86	34.4	8.8	1545
Coke added								
3¼	0.3	0.27	4.25	61.5	0.95	11.6		
3¾	0.6				0.70	8.0	16.0	
4¼	0.8	0.39	4.30	63.0	0.43	5.2		1565
4¾	1.1			63.0	0.21	2.9		
5¼	1.2	0.50	4.30	60.0	0.15	4.7	17.5	1565
				Heat 406				
0	8.8	0.56	4.50					
1	7.7	0.55						1525
Ore added								
2	3.6	0.43	4.05	43.0	1.29	33.8	10.0	
2½	1.6	0.36	4.05	52.4	1.61	20.9	13.5	1545
Coke added								
3	1.1	0.35	4.10	59.0	1.15	12.0	15.5	1565
3½	1.3	0.48	4.00	64.5	0.71	3.9	17.2	
4	1.0			65.2	0.28	1.9	18.0	1565
4½	1.2	0.50	3.90	63.4	0.22	2.4	16.2	1565

TABLE 1.—(*Continued*)

Hours after Charging	Metal, Per Cent.			Slag, Per Cent.				Temperature °C.
	Mn	P	C	MnO	P	FeO	Insoluble	
Heat 415								
0	9.7	0.56						
4	8.1	0.47						1590
Ore added								
5	0.04	0.37		51.8	0.96	26.5	9.1	1590
Coke added								
6	1.0	0.54		54.2		4.7	18.0	1575
7	2.0	0.54		51.5	0.04	2.9	19.2	1590
7½	2.2	0.39		48.5	0.03	2.1	21.7	1605
Heat 416								
0	8.7	0.56						
4	7.7	0.50						1585
Ore added								
5	0.15	0.17						1580
Coke added								
6	0.40	0.34		54.0	0.40	9.0	13.5	1580
7	0.90	0.36		51.6	0.05	2.5	19.8	1590
7½	1.20	0.50		53.0	0.05	2.0	18.8	1600
Heat 417								
0	7.0	0.56						
4	6.0	0.42						1585
Ore added								
5	0.15	0.25		41.5	0.55	43.0	5.5	1610
Coke added								
6	0.40	0.42		61.0	0.44	10.0	10.0	1600
7	1.30	0.42		61.0	0.10	6.0	14.0	1600
7½	1.10	0.45		57.5	0.07	5.5	16.0	1605
8	3.0	0.45		54.0	0.05	2.5	18.0	1605

TABLE 1.—(*Continued*)

Hours after Charging	Metal, Per Cent.			Slag, Per Cent.				Temperature ° C.
	Mn	P	C	MnO	P	FeO	Insoluble	
Heat 418								
0	5.3	0.56						
4	1.4	0.70						1580
Ore added								
5	0.05	0.16		20.5	1.60	68.0	3.0	1575
Coke added								
6	0.10	0.35		50.0	1.18	10.5	13.8	1575
7	0.40	0.56		51.5	0.55	6.0	14.8	1570
7½	0.60	0.57		48.5	0.30	5.0	15.5	1580
8	1.2	0.57		46.5	0.07	4.0	16.5	1580
Heat 419								
0	9.3	0.56						
3	6.2	0.55						1595
Ore added								
4				52.0	1.10	38.0	4.0	1595
4¼	0.4	0.40		59.0	0.95	26.0	6.0	1595
Coke added								
4¾	0.5	0.40		66.0	0.87	13.5	7.5	1570
5¾	1.0	0.42		61.0	0.70	15.0	11.0	1580
6¾	2.0	0.45		64.0	0.15	6.8	12.5	1605
7¼	2.3	0.45		62.0	0.10	5.0	15.5	1615
Heat 420								
0	8.8	0.56						
3	4.2	0.55						1585
Ore added								
4	0.5	0.25						
4¼	0.4	0.35		45.8	1.15	44.0	4.0	1585
Coke added								
4¾	0.4	0.46		41.5	0.80	12.0	7.0	1565
5¾	0.8	0.50		62.0	0.35	10.0	11.0	1585
6¾	1.1			62.5	0.20	8.4	12.0	1590
7¼	1.3	0.50		66.5	0.16	3.5	12.5	1600

TABLE 1.—(Continued)

Hours after Charging	Metal, Per Cent.			Slag, Per Cent.				Temperature °C.
	Mn	P	C	MnO	P	FeO	Insoluble	
Heat 421								
0	5.4	0.56						
3	2.1	0.90						1595
Ore added								
4	0.2			32.8				1560
4¼	0.4	0.47		36.8	1.50	44.0	4.5	
Coke added								
4¾	0.6			52.0	1.20	12.0	8.3	1570
5¾	1.2			55.2	0.15	10.0	13.0	1580
6¾	1.0			56.5	0.30	8.4	14.0	1585
7¼	0.4	0.79		52.0	0.25	3.5	14.8	1600
Heat 422								
0	8.8	0.56						
3	7.2	0.55						1595
Ore added								
4	2.7	0.40		49.5	1.67	39.8		1600
4¼	0.6	0.35		49.5	1.37	38.0	4.0	1610
Coke added								
4¾	0.7	0.45		59.5	1.00	15.0	6.5	1585
5¾	0.8	0.50		62.0	0.62	16.5	9.0	1590
6¾	1.3	0.50			0.50	11.0	11.0	1590
7¼	2.0	0.50		61.0	0.40	8.5	12.5	1590
Heat 437								
0	16.7	0.56	4.50					
2	14.1	0.54	4.47					
Ore added								
3	11.9	0.53	4.28	18.8	0.30	72.5	7.1	1545
4	0.96	0.30	3.91	52.9	0.54	35.9		1560
4½	0.40	0.16	3.23	54.3	0.72	31.5	11.4	1570
Coke added								
5½	0.31	0.36	3.06	56.5	0.46	16.1		1570
6½	0.52	0.38	3.22	62.9	0.44	12.6	11.7	1570
7	0.61	0.38	3.08	66.6	0.23	6.7	13.9	1570

TABLE 1.—(*Continued*)

Hours after Charging	Metal, Per Cent.			Slag, Per Cent.				Temperature ° C.
	Mn	P	C	MnO	P	FeO	Insoluble	
Heat 438								
0	16.1	0.56	4.50					
2	12.2	0.49	4.55					1490
Ore added								
3½	1.1	0.29	3.40	54.0	0.74	30.6	7.9	1545
4	0.49	0.32	2.74	52.8	0.76	31.4		1560
4½	0.36	0.37	1.88	50.0	0.63	32.8	8.7	1575
Coke added								
5½	0.27	0.38	1.85	59.5	0.55	31.5		1580
7	0.51	0.45	2.11	60.6	0.25	8.8	13.2	1580
Heat 441								
0	16.6	0.56	4.50					
2	14.7	0.52	3.68					1505
Ore added								
3¼	0.51		3.23		0.70	38.2	7.04	1545
3¾	0.45	0.32	2.58	51.5	0.60	35.8	8.34	1585
Coke added								
4¾	0.34	0.40	1.95	65.8	0.36	16.2	11.40	1570
5¾	0.34	0.42	2.11	66.4	0.37	14.3	11.00	1560
6¼	0.37	0.40	2.14	67.0	0.26	10.8	13.82	1560
Heat 442								
0	17.3	0.56	4.50					
2	18.4	0.45	4.52					1545
Ore added								
3	12.9	0.49	4.38	19.8	0.24	78.0	4.46	1545
4		0.32	3.92	61.1	0.56	28.3	8.18	1560
4½	2.26	0.23	3.09	61.2	0.62	23.0	10.72	1590
Coke added								
5½	0.47	0.30	3.06	66.5	0.46	15.4	17.00	1575
6½	0.77	0.37	3.00	67.3	0.30	10.2	15.90	1585

EFFECT OF TEMPERATURE ON CONTROL OF PHOSPHORUS

As one would expect from the exothermic nature of the oxidation of phosphorus, higher temperature inhibits the reaction. In heats 405 and 406, the ore was added as soon as the charge was melted. The temperatures observed at this time were comparatively low. Since the optical pyrometer was sighted on the surface of the bath, it seems likely
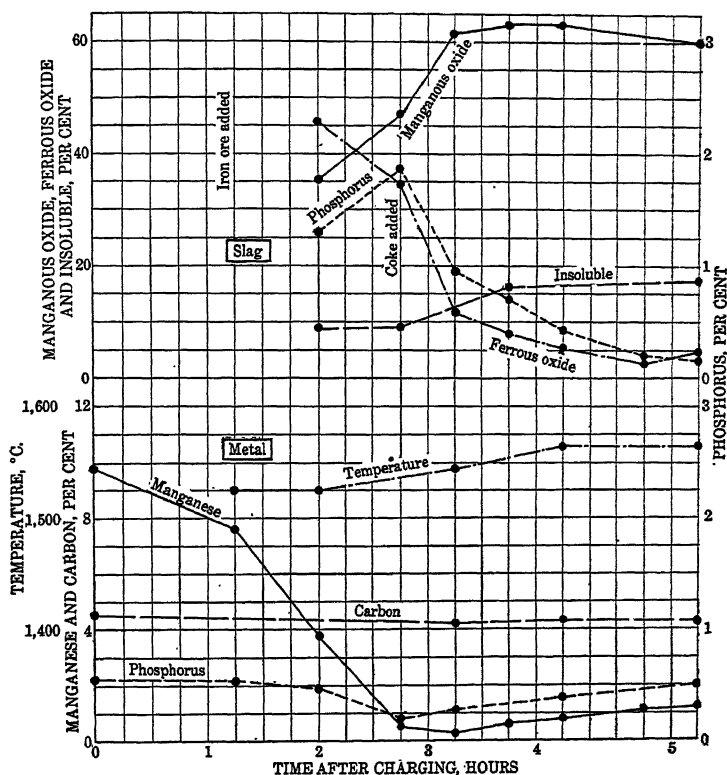
FIG. 3.—CHANGES IN COMPOSITION OF SLAG AND METAL IN HEAT 405.

that the metal was colder than these readings would indicate. The phosphorus in the slag at the time the coke was added was comparatively high in these two heats. In the other heats the charge was held longer in order to reach higher temperatures before ore was added. Although the inverse relation between phosphorus in the slag at time of adding coke and the temperature is not a smooth one, it is nevertheless apparent. The effect of temperature during the reducing and oxidizing periods of the heat when other factors were approximately constant is shown more clearly in Table 2.

TABLE 2.—*Effect of Temperature on Control of Phosphorus*

Heat Number	Phosphorus in Slag at Beginning of Reducing Period, Per Cent.	Phosphorus in Slag at Tapping, Per Cent.	Temperature at Tapping, ° C.	Insoluble at Tapping, Per Cent.
Cold Heats				
292	1.28	0.52	1525	15.2
294	1.19	0.68	1540	16.7
296	1.11	0.81	1525	15.4
303	1.21	0.68	1545	15.4
306	0.87	0.21	1585	17.6
308	0.78	0.28	1565	17.5
Av.	1.07	0.53	1541	16.3
Hot Heats				
309	0.36	0.07	1625	17.4
310	0.75	0.06	1620	20.3
312	0.75	0.17	1635	14.3
314	0.53	0.06	1600	16.8
315	0.65	0.08	1610	16.0
316	0.61	0.03	1600	18.5
317	0.84	0.11	1600	14.9
Av.	0.64	0.08	1613	16.9

RECOVERY OF MANGANESE

Manganese is generally considered to be a volatile metal. Its boiling point, as reported by Jeffries and Archer,[8] is about 1000° F. less than that of iron. By distillation under partial vacuum, almost pure manganese has been prepared by Gayler.[9] When it was proposed to treat metal containing about 15 per cent. manganese in an open-hearth furnace to slag off the manganese, the loss of manganese was suggested as a serious objection to such a scheme. A careful record was kept of material entering the furnace and of the slag and metal tapped in 193 heats, involving the treatment of about 60 tons of high-phosphorus spiegel. The spiegel was melted in lots and sampled by taking a portion of the melt just before tapping and solidification. Records of individual heats are misleading because 15 or 20 lb. of slag occupied very little space on the bottom and banks of the furnace and was often carried from

[8] Z. Jeffries and R. S. Archer: Science of Metals. New York, 1924. McGraw-Hill Book Co.

[9] M. L. V. Gayler: Preparation of Pure Manganese. *Jnl.* Iron and Steel Inst. (1927) **115**, 393.

one heat to the next. However, when a group of heats is considered, the distribution of manganese is consistent. The average distribution of manganese in 193 heats was as follows: 86.32 per cent. to the slag and 9.81 per cent. to the metal, leaving 3.87 per cent. unaccounted for.

Continuous samples of flue gases were collected over several heats to determine the amount of manganese and iron carried out of the furnace by the exhaust gases. These samples were taken by means of a water-
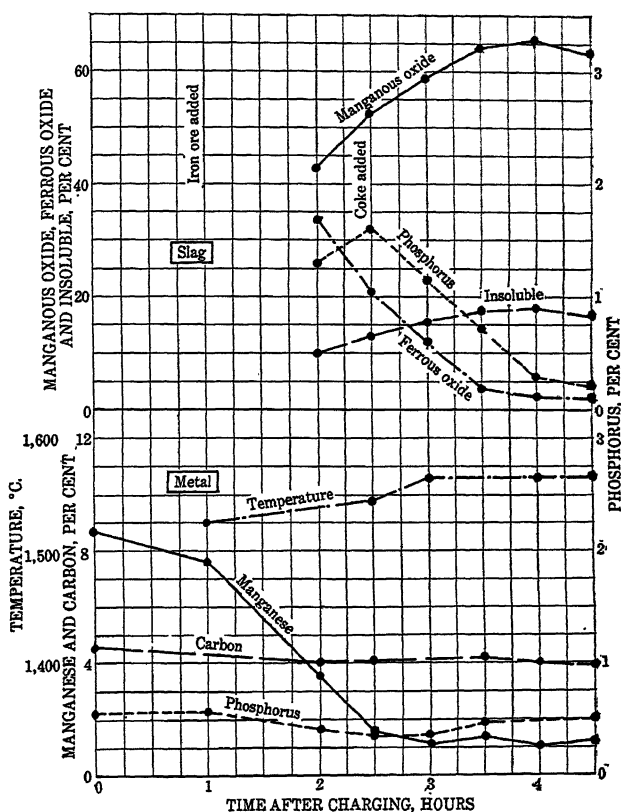
FIG. 4.—CHANGES IN COMPOSITION OF SLAG AND METAL IN HEAT 406.

cooled tube located with its center parallel to the direction of the exhaust gas coming through the port. The maximum amount of manganese recovered in dust samples represented a loss of about 1 per cent. of the manganese charged. The average for four heats was 0.66 per cent. The iron collected in the dust represented a loss of from 0.46 to 1.49 per cent. of the total iron charged. Dust samples collected from a small fraction of the total gas stream might be in error, but they indicate that the losses were small. No accumulation of dust was found in the flues. The ratio of manganese to iron in the dust samples was about

the same as in the spiegel charged, indicating that the dust represented the oxides formed by oxidation of a thin film of the metal pellets thrown up into the gases as a result of the mechanical action of the bath.

UNDERLYING METAL BATH AIDS REDUCTION OF PHOSPHORUS COMPOUNDS

It is impossible to adjust the phosphorus and iron content of high-manganese slags without reducing some manganous oxide, which results
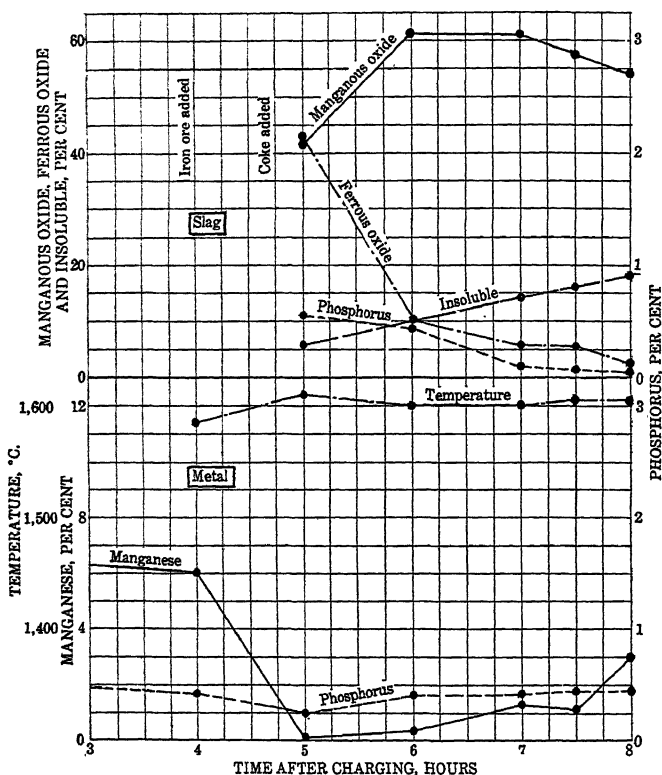
FIG. 5.—CHANGES IN COMPOSITION OF SLAG AND METAL IN HEAT 417.

in a decrease of manganese in the slag and an increase of manganese in the metal. The recovery of manganese in the slag can be increased by combining the reducing period of several heats as follows: The first charge of spiegel is ored down to slag off the manganese and the metal is tapped, leaving the high-iron slag in the furnace. A second charge of spiegel is then added, ored down, and the metal tapped, leaving slag from two charges in the furnace. A third charge of spiegel might then be added and ored down. Slag from three metal charges and the metal from the last charge would be in the furnace at this time. By adding coke, the phosphorus and the iron in the slag from three charges can be

adjusted, providing the last metal charge is in the furnace during the reducing period. The first two metal taps would contain 0.5 per cent. manganese or under, while the last one might contain 1.5 per cent. In
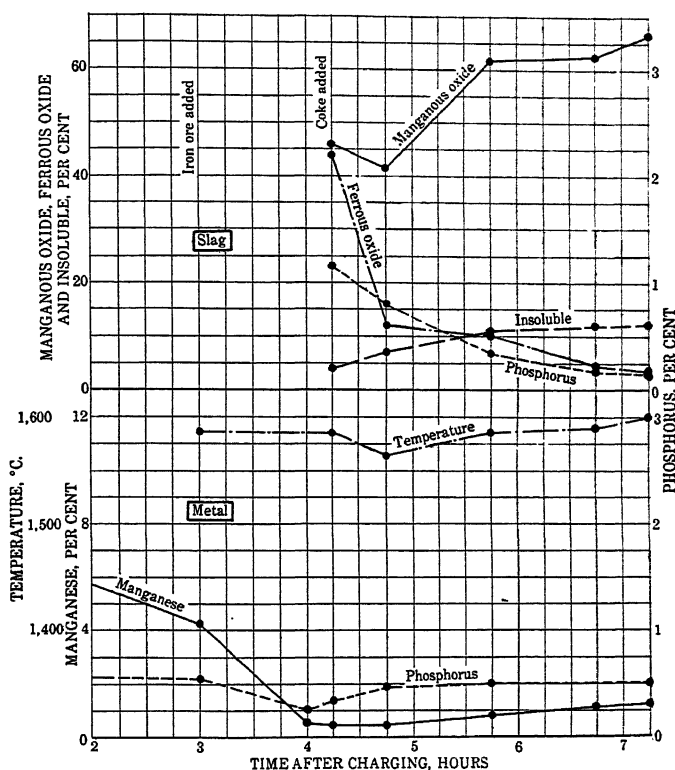
FIG. 6.—CHANGES IN COMPOSITION OF SLAG AND METAL IN HEAT 420.

addition to higher recovery of manganese in the slag, the time to treat a given amount of spiegel would be shorter and the daily tonnage larger. Space will not permit a detailed discussion of this procedure, but it has

TABLE 3.—*Average Phosphorus and FeO in the Slag*

	At Time of Adding Coke		At Time of Slag Tap		Hours under Coke
	P, Per Cent.	FeO, Per Cent.	P, Per Cent.	FeO, Per Cent.	
16 heats, slag from three spiegel charges, with no metal underneath....................	0.875	45.5	0.645	7.3	2⅔
14 single charges, with metal under slag..........................	0.95	35.5	0.14	4.1	3

been definitely established that the phosphorus in the slag cannot be reduced to proper limits unless there is a metal bath underneath the slag.   This is shown in Table 3.
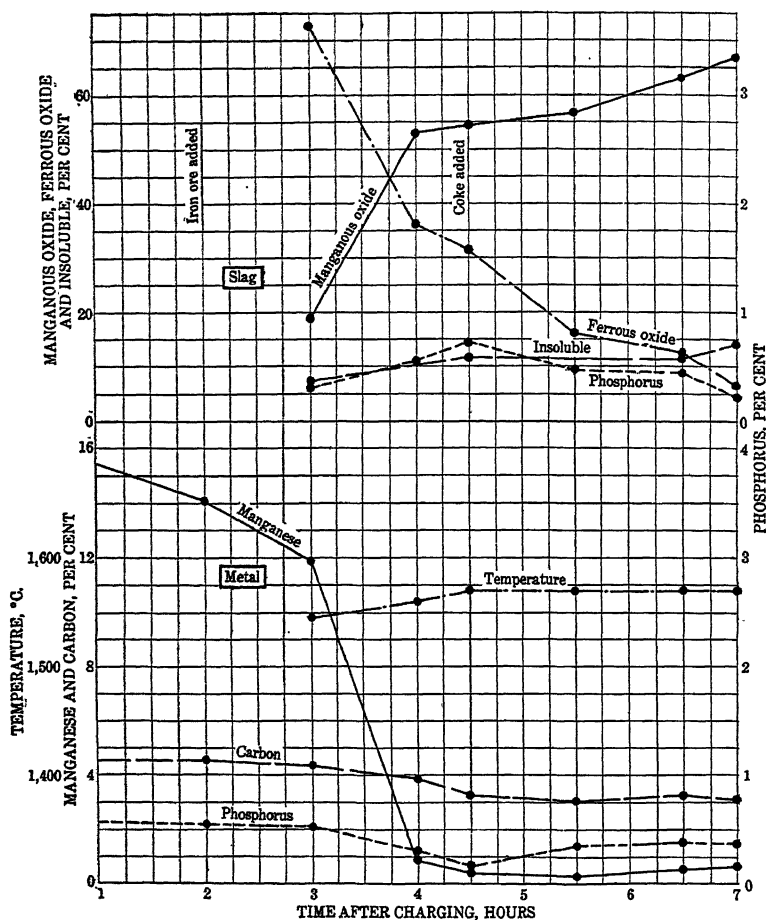
FIG. 7.—CHANGES IN COMPOSITION OF SLAG AND METAL IN HEAT 437.

COMPOSITION OF METAL PRODUCED FROM HIGH-PHOSPHORUS SPIEGEL

The production of high-manganese slag from manganiferous iron ores is an adjunct to the normal procedure for converting iron ore into steel. The composition of the metal produced from high-phosphorus spiegel is therefore important. Silicon and sulfur determinations were not made as a regular routine because the metal contained very small percentages of these elements. Most metal samples contained barely enough sulfur to report quantitatively. Silicon was also present in insignificant amounts so far as further refining of the metal into steel

is concerned.   Table 4 shows the composition of the metal from a number of heats.   The value of this metal would vary in different plants according to the quantity of it available, the size of the plant and the steel practice followed.   In a large steel plant the phosphorus content could probably be absorbed without difficulty and the very low sulfur content would be a decided advantage.

TABLE 4.—*Typical Analysis of Metal Produced from High-phosphorus Spiegel*

Mn, Per Cent.	P, Per Cent.	C, Per Cent.	S, Per Cent.	Si, Per Cent.
0.89	0.49	2.70		
0.69	0.40	3.20		
1.01	0.54	3.40		
0.36	0.30	3.30		
0.79	0.56	2.70	Varied from trace to 0.003	Varied from 0.004 to 0.048
0.65	0.38	3.59		
1.23	0.47	3.22		
0.86	0.42	3.47		
0.82	0.47	3.18		
1.21	0.50	4.32		
1.16	0.50	3.87		
0.35	0.36	3.48	0.002	0.020
0.35	0.40	3.41	0.002	0.006
1.29	0.21	3.47	0.002	0.005
1.71	0.60		0.002	0.014
0.33	0.32	3.47	0.003	0.011
Av. 0.87	0.43	3.40	0.002	0.011

PROCESS REQUIRES ONLY STANDARD EQUIPMENT

In addition to the size of the Minnesota manganiferous iron-ore deposits, ease of mining, and water transportation to steel centers, the fact that standard equipment can be used enhances the importance of these ores as a source of ferromanganese.   These deposits can be utilized quickly as a source of manganese.

EQUIPMENT NEEDED TO MEET OUR FERRO REQUIREMENTS

About 15 blast furnaces, each having a daily capacity of 400 tons of spiegel containing 15 per cent. manganese, would be required to produce sufficient high-manganese slag to manufacture 300,000 tons of ferromanganese annually.

About 120 tons of high-manganese slag could be produced from the daily output of a 400-ton spiegel furnace.   Three 50-ton open-hearth furnaces would be required to treat the 400 tons of spiegel daily.   From

the 120 tons of high-manganese slag, about 56 tons of ferro could be produced daily, or approximately 20,000 tons annually. About forty-five 50-ton open-hearth furnaces would be needed to supply 300,000 tons of ferro annually. The open-hearth capacity would be lost for general steel production, but inasmuch as one ton of metal is produced from each ton of spiegel treated, only about 40 per cent. of the blast-
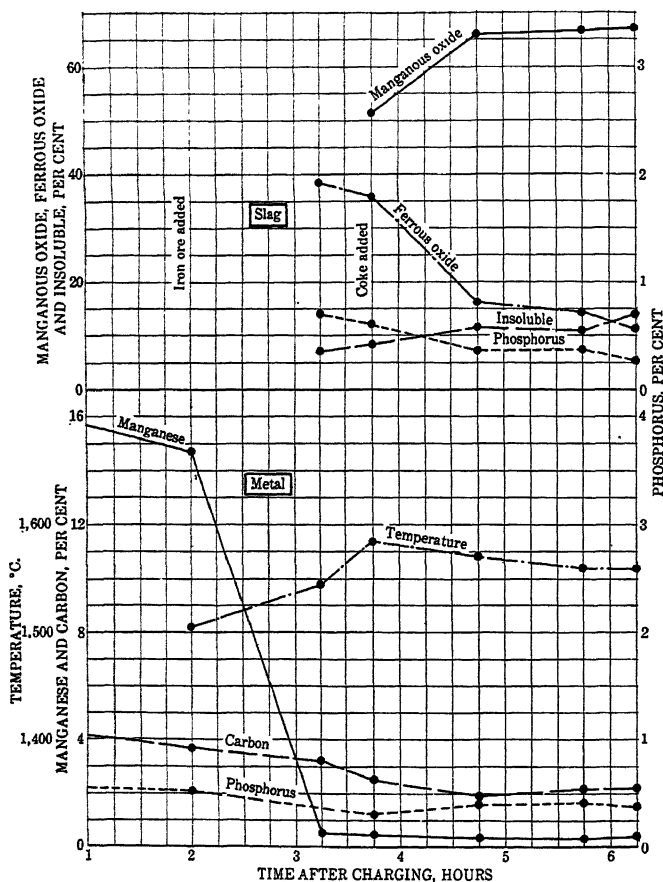
FIG. 8.—CHANGES IN COMPOSITION OF SLAG AND METAL IN HEAT 441.

furnace capacity would be lost. This loss is a result of the lower daily capacity of furnaces operating on spiegel as compared to pig iron. Only four blast furnaces and fifteen 50-ton open-hearth furnaces would be needed to meet one-third of our ferro requirements.

ELECTRIC-FURNACE TESTS

A series of preliminary tests were made at the Pittsburgh station of the Bureau of Mines to determine the relative merits of the electric

furnace and basic open-hearth furnace for producing an artificial ferro-grade ore from high-phosphorus spiegel. These tests were made in a single-phase furnace with a working capacity of 200 lb. of spiegel. The furnace was lined with a standard magnesite bottom and side walls and a silica roof.
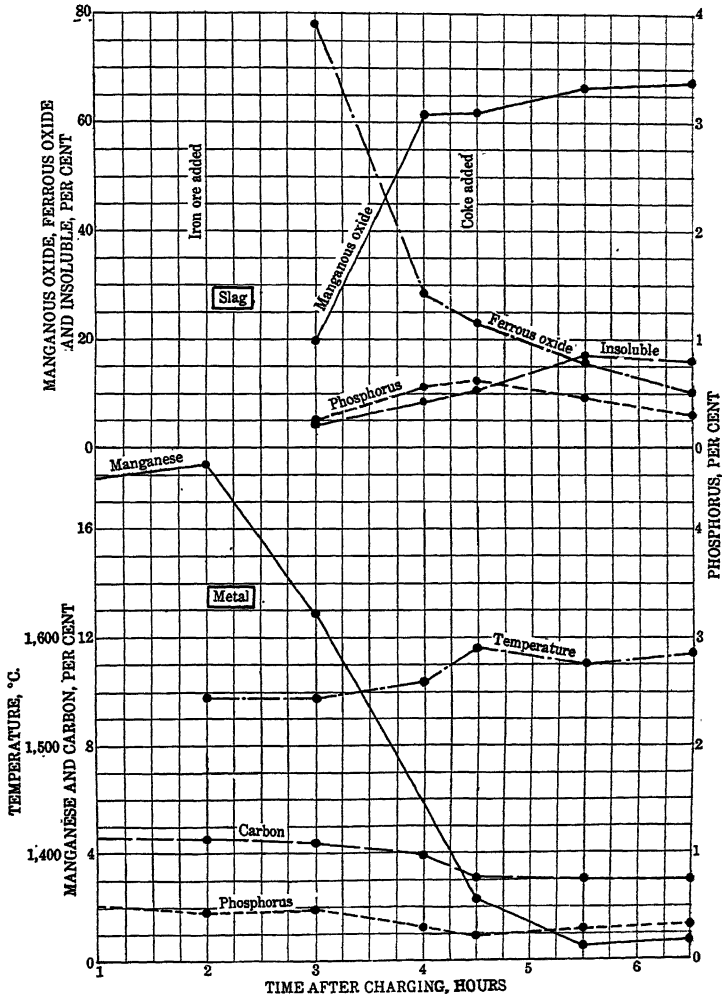
FIG. 9.—CHANGES IN COMPOSITION OF SLAG AND METAL IN HEAT 442.

The procedure followed was in general the same as for the open hearth. Cold spiegel was charged; after it was melted, iron ore was added. Figs. 10 to 12, inclusive, and Table 5 show the the changes in slag and metal composition throughout several heats. The time required to make a heat was less in the electric furnace. This is due to the more

TABLE 5.—*Changes in Composition of Slag and Metal in Electric-furnace Heats*

Time After Charging, Minutes	Percentage Composition						
	Slag				Metal		
	FeO	MnO	SiO$_2$	P	C	Mn	P
Heat 4							
60					4.5	11.5	0.55
105	38.2	45.6	9.26	1.28	4.31	0.57	0.42
115	55.9	29.5	8.6	0.67	4.12	1.40	0.26
135	32.2	49.7	8.87	1.35	4.24	0.57	0.32
185	20.9	59.5	10.2	1.37	3.97	0.48	0.31
200	14.2	58.8	11.7	1.10	3.85	0.61	0.43
Heat 5							
50					4.5	11.5	0.55
80	58.1	21.3	8.36	0.58	4.41	6.5	0.43
105	31.2	40.9	8.72	1.11	4.02	1.34	0.30
115	25.4	44.6	9.76	0.94	3.80	0.76	0.38
135	14.1	46.3	14.9	0.59	3.54	0.78	0.48
150	11.1	47.8	15.8	0.37	3.51	1.27	0.52
Heat 6							
45					4.5	11.5	0.55
80	67.3	15.5	9.64	0.30			
115	23.4	58.9	9.80	0.95	3.51	0.55	0.33
130	14.2	63.0	12.7	0.39	3.85	1.44	0.52
150	9.15	65.3	15.6	0.19	3.55	2.07	0.57
Heat 7							
65					4.5	11.5	0.55
130	25.5	51.5	10.3	1.18	4.24	0.66	0.28
150	16.9	55.5	13.6	1.01	4.19	0.60	0.39
165	14.7	58.9	13.4	0.96	4.00	0.61	0.41
185	13.2	60.0	14.3	0.84	3.88	0.92	0.48
200	9.7	59.1	16.6	0.27	3.85	2.40	0.54
Heat 8							
70					4.5	11.5	0.55
110					4.30	3.06	0.33
125	25.8	58.6	8.10	0.81	3.87	0.92	0.41
135	21.7	60.8	9.62	0.51	3.54	1.20	0.45
155	9.11	65.3	14.5	0.12	3.13	2.42	0.41
165	5.85	55.0	17.0	0.05	3.25	3.36	0.53
185	3.64	52.7	19.7	0.04	3.11	3.82	0.53
Heat 9							
30					4.5	11.5	0.55
85	20.9	59.4	10.7	0.68	3.95	1.48	0.43
100	17.5	55.5	12.0	0.55	3.66	1.30	0.46
120	10.5	60.1	14.6	0.19	3.50	2.30	0.52
140	6.53	60.7	17.0	0.05	3.38	3.22	0.52
160	4.76	58.4	17.9	0.05	3.48	3.92	0.55

strongly reducing atmosphere that can be maintained in the electric furnace during the adjustment of the phosphorus and iron content of the slag. If molten spiegel were charged and ore added shortly thereafter, it would require from 1½ to 2 hr. to complete the entire treatment in the electric furnace as compared to 3½ to 4 hr. in the open hearth. The slag could be removed from the electric furnace by hand rabbling just before tapping. A cleaner separation of slag and metal could be
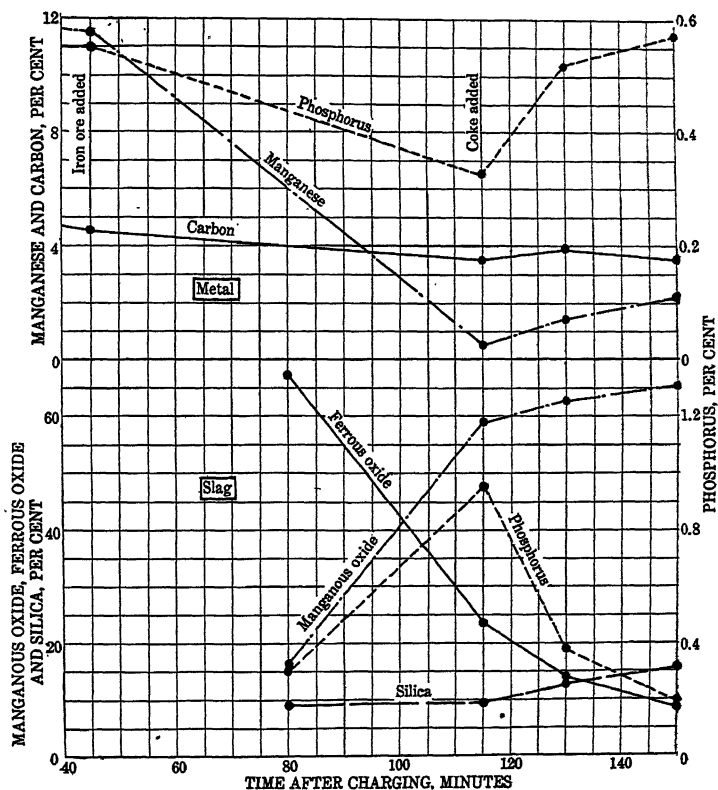
FIG. 10.—CHANGES IN COMPOSITION OF SLAG AND METAL IN HEAT 6.

made in this way. This would also tend to preserve the bottom of the furnace by preventing contact with the slag.

It was necessary to add silica in the electric furnace just as it was in the open hearth. From 14 to 16 per cent. SiO_2 seemed necessary to get proper adjustment of phosphorus and iron in the slag and a clean separation of slag and metal. These preliminary tests indicated that slag containing 58 to 65 per cent. MnO, 7 to 10 per cent. FeO, 14 to 16 per cent. SiO_2, and 0.15 to 0.2 per cent. phosphorus can be made with regularity and certainty. A balance of the manganese indicates 77 to ·82 per cent. can be recovered in the slag, 14 to 16 per cent. in the metal,

with only a few per cent. unaccounted for. With judicious operation, the loss of manganese should be small.

The data shown in Fig. 23 and Table 6 indicate that the metal will contain about 2.0 per cent. manganese when the phosphorus in the slag has been reduced to about 0.2 per cent. The amount of manganese recovered in the slag probably could be increased as follows: Tap the metal from the first charge as soon as the manganese is oxidized, but leave the slag which would be high in iron and phosphorus, in the furnace.
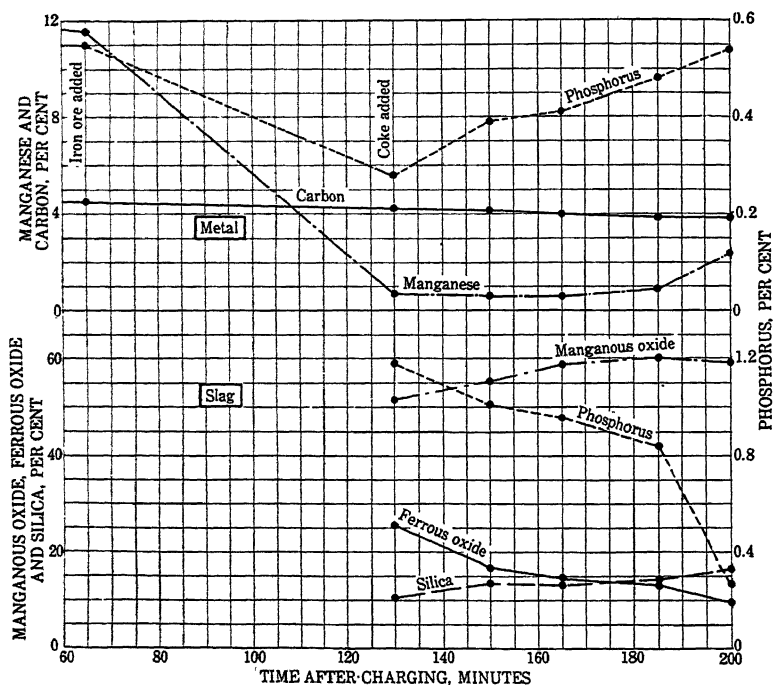
FIG. 11.—CHANGES IN COMPOSITION OF SLAG AND METAL IN HEAT 7.

Charge the second metal, ore down, and add coke to adjust the phosphorus and iron in the slag from two heats. The first metal would contain less than 0.5 per cent. manganese, and it seems likely that the second charge would not necessarily contain more than 2 per cent. manganese. Just how far such a procedure could be carried has not been determined, but it seems certain that more of the manganese could be recovered in the slag by some such method.

With a standard magnesite bottom there was little corrosion of the bottom or side walls in either the open-hearth or electric-furnace tests. The addition of manganese is generally considered as a means of increasing slag fluidity, but in the range of composition of interest in this work the slags were viscous unless silica was arbitrarily added
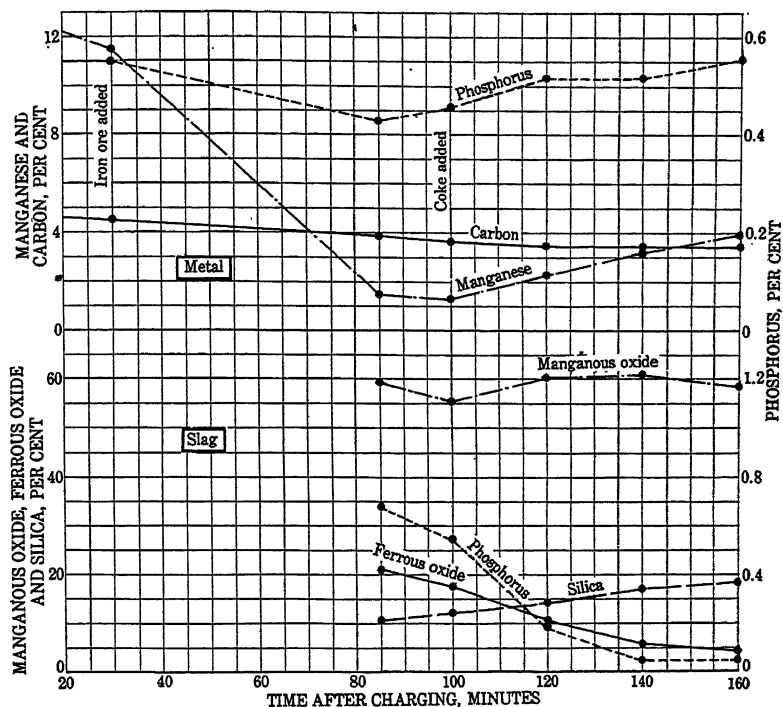
FIG. 12.—CHANGES IN COMPOSITION OF SLAG AND METAL IN HEAT 9.

TABLE 6.—*Relation between Manganese in Metal and Phosphorus in Slag*

Phosphorus in Slag, Per Cent.	Manganese in Metal, Per Cent.	Phosphorus in Slag, Per Cent.	Manganese in Metal, Per Cent.
0.04	3.82	0.67	0.92
0.05	3.92	0.81	0.92
0.05	3.36	0.84	0.92
0.05	3.22	0.94	0.76
0.08	2.50	0.95	0.61
0.12	2.42	0.96	0.55
0.19	2.30	1.01	0.60
0.19	2.07	1.10	0.61
0.27	2.40	1.18	0.66
0.37	1.27	1.18	0.41
0.39	1.44	1.28	0.57
0.48	0.81	1.35	0.57
0.51	1.20	1.37	0.48
0.55	1.30	1.45	0.37
0.59	0.78		

to thin them.   There was some trouble in the open hearth from building up on the bottom.   In the electric-furnace tests a slight corrosion of the side walls took place at the slag line.
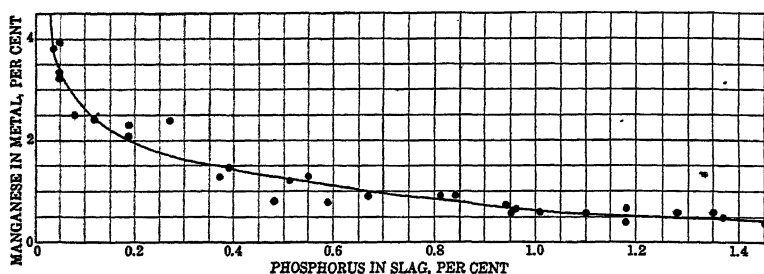
FIG. 13.—RELATION BETWEEN MANGANESE IN METAL AND PHOSPHORUS IN SLAG.

SUMMARY

Tests conducted with a 6-ton blast furnace indicate that a charge of 100 per cent. manganiferous iron ore can be melted successfully. Such an ore charge would produce high-phosphorus spiegel containing from 10 to 15 per cent. manganese and about 0.5 per cent. phosphorus. The manganese can be separated from the phosphorus and iron in this type of metal by treating it in a standard basic open-hearth furnace or an electric furnace.   By adding iron ore most of the manganese, together with some of the phosphorus, is oxidized and passes into the slag.   At this point the slag is composed largely of FeO and MnO.   The FeO and the phosphorus compounds can be reduced much more rapidly than the MnO by covering the slag with a layer of coke.   By holding the slag under a layer of coke for about 3 hr. in the open hearth and 1 hr. in the electric furnace the FeO and phosphorus can be reduced to amounts permissible in ferro-grade materials.   As the FeO is reduced, low-silica slags become very viscous, but this can be overcome by adding silica or regulating the silica in the iron ore.   Silica in the slag is objectionable, but no other effective cheap thinning material has been found.   Changes in the composition of the slag and metal of open-hearth and electric-furnace heats are shown graphically.

These experiments are significant because they indicate that large quantities of ferromanganese can be made from Minnesota manganiferous iron ores.   The method can be turned to quickly and a large part of our ferro requirements can be met without serious loss of equipment needed for the production of steel.

DISCUSSION

G. B. WATERHOUSE, Cambridge, Mass.—Did you bring out the percentage of manganese possible in the alloy?

T. L. JOSEPH.—It would be possible to make an 80 per cent. alloy. In most of the cases cited, the manganese and iron had a ratio in the final slag of about nine to one.

G. E. THACKRAY, Johnstown, Pa.—Have your experiments gone far enough to give some indication of the comparative cost of producing ferro in this manner as compared with the practice of the past?

T. L. JOSEPH.—The only way I can answer that is as follows: As I pointed out, approximately 0.3 ton of slag and 1 ton of metal are produced for every ton of spiegel treated. If we assume that the metal of the composition shown is worth approximately the same as hot metal in the steel plant, one ton of this slag can be produced for between $25 and $30. You can get almost any figures you want, depending upon the value assumed for the hot metal.

For example, I think that 1 ton of metal and ⅓ ton of slag can be produced for about $23. If the metal is worth, say $16, that leaves $7 for 0.3 ton of slag containing around 45 or 50 per cent. of manganese. I am assuming now that this operation is carried out by a company that owns the ore and can deliver the manganiferous ore to its furnaces for something like $3.50 per ton. Figuring it through as best I have been able to do, the cost of the slag will be in that range—$25 to $30 per ton. Since the cost of the slag per ton is in the range of the cost of manganese ore at present, it seems that ferro could be made from this slag at a cost approaching the cost in normal practice.

J. T. MACKENZIE, Birmingham, Ala.—I wonder if Mr. Joseph has considered the scheme used with high-phosphorus iron. The problem there, of course, is to make the steel from 0.80 phosphorus down to 0.05, or whatever the specifications may be, and also to produce a slag with a minimum of 18 per cent. P_2O_5. That is done by putting slag on the metal which reduces it to 0.10 per cent. P, which occurs very readily and then, by changing the slag, taking it on down from 0.10 to 0.05 per cent. P. In this same furnace, they pour the steel out from under the slag, put the new metal in with this old slag, and accomplish the same reduction, which also builds up the phosphorus to the required point in the slag. It might be that some such operation as that would reduce the cost considerably, as I know has been done with phosphoric slag.

T. L. JOSEPH.—That is an interesting suggestion. I think it would greatly reduce the cost of the operation. Something like that could be worked out.

C. H. HERTY, JR., Pittsburgh, Pa.—I think Mr. Joseph mentioned something of that in his paper, where he said that he had made a melt and obtained high-manganese slag, left the slag in the furnace and put in a fresh charge of spiegel. That is about the same thing.

W. J. McCAUGHEY, Columbus, Ohio.—Did Mr. Joseph notice any effect of the high-manganese slag on the bottom material?

T. L. JOSEPH.—Our trouble is keeping the slag fluid. Manganese is considered as an agent for producing fluid slags. It does produce such slags providing sufficient silica is present but when slags run as high as 60 per cent. in MnO and you try to keep the silica down around 10 per cent., you have a difficult slag to deal with. Our slags tended to build up the bottom.

W. J. McCAUGHEY.—There is a reason for that mineralogically. Manganese oxide (manganosite) and the magnesium oxide (periclase) are isomorphous. Both form cubic crystals and are end members of a series of solid solutions. For instance

the periclases formed in nature have in them up to 9 per cent. of manganese oxide. I wonder if the manganous oxide in the slag might not pass into the bottom material, where it would be kept in solid solution in the MgO (periclase) which forms the essential constituent of magnesite bottoms?

T. L. JOSEPH.—When we change the bottom of the furnace we find that the new bottom absorbs a large amount of slag.

G. B. WATERHOUSE.—The suggestion, though, is that if you analyze the bottom material when you make a new bottom you will find a great deal of manganese oxide in the old bottom material.

T. L. JOSEPH.—Undoubtedly that would be the case.

[A discussion by H. O. Chute, with a reply by T. L. Joseph, was published in *Mining and Metallurgy*, May, 1930, page 278.]

Beneficiation of Iron Ore

Round Table

(Chicago Meeting, September, 1930)

THE following discussion occurred on the afternoon of Sept. 22, 1930, as part of the fall meeting of the Iron and Steel Division at Chicago. About seventy-five men attended this session. C. B. Murray opened the meeting, as follows:

C. B. MURRAY, Cleveland, Ohio.—It is very encouraging to see so many here this afternoon to discuss this important matter of beneficiation. The producers of ore, I am sure, are anxious to furnish the grade of ore that the consumer wants. The consumer sometimes wants that which cannot be economically produced and often the producer cannot understand why the consumer wants certain things. It was to bring together these two interested parties that this meeting was proposed.

I was appointed the chairman of the meeting, chiefly because I happened to be the chairman of the Iron Ore Committee of the Institute. I know a little about iron ore but have not perhaps kept up with the times in blast-furnace practice. I am asking Mr. Sweetser, who is well informed from both sides, to take over the meeting and carry on the discussion.

R. H. SWEETSER, Columbus, Ohio.—We want to have a free discussion between the iron-ore men and the blast-furnace men as to just what we are trying to reach in the beneficiation of iron ores. Many of those present have had a great deal of experience. There are men here from the ranges who have been passing through the experimental stage of beneficiation of iron ores, and there are some who have already gone on to commercial production. We have reached the point where the beneficiation of iron ore is important to the whole iron and steel industry. The connection between iron-ore beneficiation and the cleaning of coal is so close that I think we can profit by working very close to the coal people.

SOME ASPECTS OF THE IRON-ORE SITUATION

W. G. SWART, Babbitt, Minn.—I was very much interested in Mr. Richards'[*] paper on tonnages and the 20-year life. There is one interesting thing about the ore reserves; that is, the irregular distribution of that tonnage. On the Mesabi Range, for example, the United States Steel Corpn. owns between 70 and 75 per cent. of the reserve tonnage. They ship between 40 and 50 per cent. of the annual Lake Superior

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[*] F. B. Richards: Some Aspects of the Iron-ore Situation. *Min. & Met.* (1930) 11, 437.

output. Therefore, saying it is 50 per cent., their 50 per cent. comes out of 70 per cent. of the reserves, whereas the independents' 50 per cent. comes out of 30 per cent. of the reserves. Therefore, the irregular distribution means that while some people have plenty and are going to see a life of perhaps 40 or 50 years without any trouble, there must be others who have very much more limited life.

Further than that, the United States Steel Corpn. has its ore all in one control, whereas the independents have theirs in perhaps 10 or 15 different hands.

Trading has been common in the past, but those people who now sit tight on nice high-grade ore are not so willing to trade. The United States Steel Corpn. is to be admired for having the courage and the vision to put together the ore reserves that it has. It is a wonderful bundle of ore. There is nothing like it in this country that I know anything about.

As far as the beneficiation processes are concerned, I do not think anyone can look into the future far enough to tell which of the processes is going to survive. Possibly all of them will. No one process is applicable to all ores, by any means. The ores even vary in the washing processes. There are great variations in the plants now running. I know one plant that has recently been built and another is to be built alongside it for an ore which from all appearances is of the same general class as the first, yet the two do not behave at all alike in the mill. Therefore the mills have to be suited to the ore and equipment has to be furnished to handle the particular problem in hand. In any mine of considerable size there are six or eight or more different kinds of ore to be handled. The plants try to mix them and try to get an average; in some cases they put two or three units in a mill to handle these different grades of material separately. I have no great doubt about the outcome; I think the beneficiation of ore is not only coming, it is here.

The Mesabi Range, for instance, produced last year 43,000,000 tons, of which 6,000,000 tons were washed ore. I am talking of the Mesabi Range because that is where most of this work has been done, where it has been applicable and where it has been needed.

Of course, I am not so competent to talk about the future of it from a blast-furnace man's standpoint, except what I learn from the blast-furnace people. The beneficiated ores seem desirable not so much because of their analysis but because of their better structure, giving higher yields in the blast furnace.

A very interesting thing happened through the period of depression, since the prices were cut in 1924 on iron ore; that is, that the underground mines on the Mesabi Range, and somewhat on the other ranges, too, although not so much, were nearly closed down, but every washing plant went right along, with one or two local exceptions, showing that in all probability the washing plants were strongly competitive even on an equal price.

The Blast-furnace Viewpoint

T. T. Read, New York, N Y. (written discussion).—As indicated in the reported discussion between Mr. Sweetser and Dean Appleby,[*] what is most needed in the solution of these problems is not only more data but more accurate data. This may be illustrated by further analysis of the comparison of the Columbus, 1930, operating data with the Dover, 1897, data. Assuming that the 4.43 per cent. SiO_2 in the coke, as given in the analysis quoted, is all right (though it seems rather low for a 12.42 per cent. of ash coke) the Dover furnace had, per ton of pig iron, 73 lb. SiO_2 in the coke and 132 in the ore burden, or a total of 205 lb. SiO_2. Mr. Sweetser

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[*] R. H. Sweetser: Beneficiation of Iron Ores from the Blast-furnace Viewpoint. *Min. & Met.* (1930) **11**, 423.

does not give the SiO_2 content of his coke ash nor of his ore mixture. Giving him the benefit of the doubt that the ratio of SiO_2 to total ash was the same in both cases, we can estimate that the SiO_2 in his coke was 48 lb., and if his ore-coke ratio was the same and the ore mixture was 8 per cent. SiO_2 it would contain 176 lb. SiO_2, thus making a total of 224 lb. SiO_2. From this it would appear that the decreased ash content of the coke has not compensated for the increase in SiO_2 content of the ore; the Columbus furnace shows nearly a 10 per cent. increase in the total SiO_2 per ton of pig iron. Since the ore-coke ratio exceeds 2 to 1 we would naturally expect that the percentage change in the coke analysis would have to be more than double that in the ore analysis to compensate.

It is interesting to note that Mr. Reese, in the article quoted, evidently thought the reason for adding SiO_2 to the charge was to bring up the Si content of the pig iron, not to bring the S down; the latter he evidently considered was governed by the amount of stone used. As Mr. Ferguson points out, the 200° F. higher blast temperature at the Columbus furnace makes a world of difference, as it would raise the silicon content of the pig iron and lower its sulfur content. On the face of the data available, it appears that the Columbus furnace has a larger ratio of slag to pig iron than the Dover furnace had and that if the Dover furnace had had as hot a blast as the Columbus furnace has it could have operated with a smaller slag volume and still kept the Si content of the pig iron up and the S content down.

One thing that we need is a surer grasp of the relation of increase in the ratio of fuel to burden, increase of blast temperature and increase in the Ca-Mg content of the slag (raised melting point) to their joint effects on hearth temperature, silicon content and sulfur content of the pig. Howe indicated[1] their qualitative relation by $+$ and $-$ signs, but if anybody has published any definite quantitative data on it I have not seen it. The experimental data Joseph has published indicate that the slag of a modern blast furnace would remove much more sulfur from the metal if it had a better chance to do the job. It seems to me that instead of shooting at the double bull's-eye of trying to make the silicon content and the sulfur content of his pig right in one operation, it is possible that it might pay the blast-furnace operator better to run for a proper silicon content and if his sulfur is too high to wash the metal outside with a high-lime slag, as some of the old patents proposed to do. Neither do I know anything sacred about the 3.5 to 4.5 per cent. carbon content of ordinary pig iron; people are making a 2 per cent. carbon pig iron in the cupola, why cannot it be done in the blast furnace and what would be the effect of the change on the other phases of the operation? The melting point of the metal would probably go up about 200° C., but what of it? Who knows, and why are we afraid to spend some money on trying to find out?

Mr. Warner, in making out a good case for the St. Lawrence waterway, suggests that as the SiO_2 content of Lake Superior ores continues to go up it will pay to bring in high-grade foreign ores instead of using more fuel to smelt a charge higher in SiO_2. If his argument is really sound (and we lack the precise data to either refute or support it) it will be, I believe, because the increased coke necessary will put too much sulfur in the pig iron and not because it will be cheaper to import higher grade ore rather than to use more coke per ton of pig iron. But Joseph's results indicate that the slag does not now carry all the sulfur it could; if we can make it carry more there may be no limit, except fuel cost, to the amount of coke we can use per ton of pig iron. No matter what angle all these problems are studied from we see always the same need; more data and more accurate data.

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[1] H. M. Howe: Iron, Steel, and Other Alloys, Ed. 2, Table 19. Cambridge, 1906, A. Sauveur.

R. H. SWEETSER (written discussion).—Dr. Read says "what is most needed in the solution of these problems is not only more data but more accurate data." I agree with him, fully.

Dr. Read in his "further analysis of the comparison of the Columbus, 1930, operating data with the Dover, 1897, data," says that it would appear that "the decreased ash content of the coke has not compensated for the increase in SiO_2 content of the ore." What I actually said was: "It appears, therefore, that the increased silica in the ores, generally, has been counterbalanced by a corresponding decrease in the percentage of ash in the coke, and by the progress made in the art of smelting iron ores." And I still stick to it.

Dover furnace used only 1664 lb. of coke per ton of pig iron in 1896, at a period when most blast furnaces were using more than 1 lb. of coke per pound of pig iron. Columbus furnace used only 1586 lb. of coke per ton of pig iron, 24 years later, using an ore mixture with 2.28 per cent. more silica than in the Dover ore mixture. From the figures presented, I drew the conclusion that the handicap of increased silica in our ore mixtures had been counterbalanced by a corresponding decrease in the percentage of ash in our cokes, "*and by the progress made in the art of smelting iron ores.*" The art of making merchant pig iron these days, with its pentagonal specifications, is far in advance of the art of making Bessemer pig iron in the middle nineties, with its

TABLE 1.—*Comparison of Furnaces*

	Dover		Columbus	
	Per Cent.	Lb. per Ton Pig Iron	Per Cent.	Lb. per Ton Pig Iron
SiO_2 in ore mixture.................	6.00	220.26	8.28	321.92
SiO_2 in coke.......................	4.43	73.71	4.10	65.02
SiO_2 in limestone...................	5.44	41.94	2.05	12.71
Total SiO_2 per ton pig iron.........	....	335.91	....	399.65
Ore.................................	....	3761	....	3888
Coke................................	....	1664	....	1586
Limestone...........................	....	771	....	620
Total materials....................	....	6196	....	6094
Silicon in pig iron..................	1.23	27.55	2.02	45.25
Silica in pig iron...................	2.61	58.60	4.29	96.23

	POUNDS
Total SiO_2 per ton pig iron at Columbus....................	399.65
Total SiO_2 per ton pig iron at Dover.......................	335.91
Total excess SiO_2 at Columbus.............................	63.74
Extra SiO_2 needed for Columbus pig iron...................	37.63
Extra silica in Columbus slag.............................	26.11

SLAG ANALYSIS

	DOVER, PER CENT.	COLUMBUS, PER CENT.
Average SiO_2...	34.37	36.93
Average Al_2O_3...	15.37	13.66
Average CaO...	43.13	
Average MgO...	4.74	
Total SiO_2 plus Al_2O_3.................................	49.74	50.59
Total CaO plus MgO.....................................	47.87	

liberal limits for silicon and 0.050 per cent. for sulfur, as the only specifications for which the furnaceman was responsible. In this case a man making Bessemer iron would set his furnace, and then practically go off and forget it, because he would not have to worry about the manganese or phosphorus, and the silica could be anything from 1 per cent. up to 1.5 per cent., and all he would have to do would be to keep the sulfur under 0.050.

The increase of fixed carbon in the coke from 83.12 per cent. at Dover to 90.07 per cent. at Columbus is the greatest factor in the better fuel economy. Dr. Read could not reconcile 12.42 per cent. ash with only 4.43 per cent. silica in the Dover coke; and neither can I. I do not understand how such a low silica content could have been reported, but that is according to the paper published in the *Transactions*.[2] That is all I had to go by. The silica in the Columbus coke was 4.10 per cent. and the ash 8.65 per cent.; the moisture in the coke was about 1.00 per cent. The Columbus coke was filled by volume in skip cars balanced against railroad weights; the Dover coke was all weighed in coke buggies, necessarily with varying amounts of moisture through the winter months of November to April inclusive. A further comparison of the two furnaces is given in Table 1.

Evidently Mr. Read has made a miscalculation in his figure on SiO_2. I called his attention to it the other day, and he said he would get it corrected. He has the total as 200, but Dover has 335.9 lb. of silica.

The table shows that there were 26 lb. more silica at Columbus to take care of in the slag.

The sulfur and silicon in the two pig irons are given in the paper. It was 0.034 per cent. sulfur at Dover and 0.027 per cent. at Columbus. I still maintain that the increased silica in our mixtures is going to be compensated by increased blast-furnace efficiency and decrease in coke ash.

T. T. READ (written discussion).—I am grateful to Mr. Sweetser for his reply to my discussion, for he has calculated out the quantities involved more accurately, thus permitting a better comparison of what the two furnaces were doing. Like Mr. Sweetser, I still stick to my argument, and maintain that the figures given in his discussion, which show that the Columbus furnace is handling (in round figures) 400 lb. SiO_2 per ton of pig iron made while the Dover furnace was handling 336 lb. per ton of pig iron, check my assertion that the Columbus furnace is handling 19 per cent. more silica per ton of pig iron to be disposed of in slag, since, when the allowance for the higher silicon content of the Columbus pig iron is made, the extra SiO_2 going into the slag is 26 lb., or 9 per cent. increase over the 293 lb. SiO_2 per ton of pig iron the Dover furnace was handling into slag. And since 65 lb. SiO_2 in the coke at Columbus is only 8.7 lb. less than the 73.7 lb. in the coke at Dover, while the 322 lb. SiO_2 in the Columbus ore is almost 120 lb. more than the 220 lb. in the Dover ore, I still maintain that the decreased silica in the better coke has not compensated for the increase of silica in the ore mixture. However, our apparent disagreement is in the use of words rather than in ideas. If we can modify our language so as to say that better coke and better furnace practice have made it possible to handle an increased amount of total SiO_2 in the furnace burden without increasing the coke required, we will be in absolute agreement. I will, however, ascribe the result chiefly to better practice, namely, the hotter blast, rather than to the decreased silica content of the coke.

C. E. WILLIAMS, Columbus, Ohio.—Dr. Read brought out another suggestion to the effect that since our blast-furnace operation is designed to produce a definite

[2] A. K. Reese: Notes on Six Months' Working of Dover Furnace, Canal Dover, Ohio. *Trans*. A. I. M. E. (1897) **27**, 477–85.

silicon and a low sulfur content in one operation, it might be possible to produce an iron of the desired silicon content, paying no attention to sulfur, and then to desulfurize the metal in a separate furnace. He quotes Mr. Joseph's results to the effect that present blast-furnace slags could carry more sulfur, and therefore under suitable conditions could desulfurize the iron to greater advantage. As a result, less coke could be used in producing a lower sulfur metal, and therefore the rising silica content of the ores would be counteracted by the smaller amount of ash charged. This is an interesting suggestion and a subject for much speculation.

T. L. JOSEPH, Minneapolis, Minn.—I might mention that the reason we think the blast-furnace slag might carry more sulfur than it does is that some experiments on a small scale showed that desulfurization seems to be a sort of washing effect. The amount of contact is very important; that is, we took high-sulfur metal and brought it in contact with a layer of slag at about 1500° C. and in two hours removed the same amount of sulfur that was removed in a few minutes by dropping the metal as fine shot down through the same amount of slag. So we think, from those results, that better desulfurization would result from greater contact between the slag and metal in the blast furnace. A deeper layer of metal or slag might be needed to get this advantage.

IMPROVEMENTS RESULTING FROM BENEFICIATION

J. A. MacKILLICAN, Hibbing, Minn.—While the purpose of this meeting is to discuss the beneficiation of iron ore, I do not wish to say anything at this time about this particular subject, but I do wish to discuss the improvement in the structure of the ore as a result of beneficiation. The washed and jigged ores now being shipped from the Mesabi Range are much superior in structure to the old range ores, and I suggest that these beneficiated ores be given the same differential as those shipped from the old ranges.

The results of a large number of cargo screen tests made on our Hoadley grade ore for the year 1930 average as follows:

	PER CENT.		PER CENT.
Held on 8	64.4	Held on 80	2.5
20	11.1	100	1.5
40	11.3	Through 100	3.2
60	6.0		100.0

I believe this ore is considerably better in structure on all of the various sizes than the old range ore; therefore it seems to me that it would be in order for the consumers of ore to pay more for a beneficiated ore, on account of the structure, because it promotes the efficiency of the blast furnace materially. The structure is relatively constant, therefore it would be in order for a producer of beneficiated ore to guarantee the structure in exactly the same manner as the analysis is guaranteed. It would be reasonable to ask the consumer of ore to pay at least the old range differential for a beneficiated ore of such a desirable structure.

W. A. HAVEN, Cleveland, Ohio.—Mr. MacKillican's suggestion regarding a higher price for washed ores might be rather hard to realize. There is no question that some of the washed Mesabi ores physically are the full equivalent of some of the old range ores. In my 20 years of blast-furnace operating experience, I might say that I have had to do with certain washed Mesabi ores which I would prefer to many old range ores that I have used. Some of the ores that come to mind are the Mace and the York. They are very nice working Mesabi ores which are prepared by washing. It is with-

out doubt a fact that such ores contribute largely to good furnace operation and, if they have the same amount of iron in them, are worth much more to a furnace operator than an excessively fine ore such as Mahoning, or Group 2, or ores of that nature. The reason is very clear, because we know that very fine ores may be subject to a loss of as much as 10 per cent. between the time they are charged in the furnace and the time that they reach the bottom.

Whether or not it would be possible to get any companies producing pig iron to pay the difference between the market value of the old range and the Mesabi ores is hard to say, but I would think it very unlikely, for the reason that most of the corporations use ores that they own. These are delivered to the blast-furnace operator, and he has very little choice.

However, it would seem that producers who are more or less dependent upon outside producers of ore for their requirements could certainly, very wisely, be careful in selecting the ores which they buy, because if they buy them at the market rates, they have an opportunity of profiting by that differential in value between a washed Mesabi and a Mesabi that has not had the benefit of washing.

Mr. Richards' paper, it seemed to me, would have been a little clearer if he had qualified what he considered the nature of the ores which he had lumped into the possible reserves. It is hard to say these days what ore should go into a reserve and what should not. No mention was made of that fact. Some of the ore-mining people might well add that to the paper which Mr. Richards has written.

IMPROVEMENT IN BLAST-FURNACE OPERATION

I was interested in Dr. Read's comments with regard to Mr. Sweetser's paper, and I think I can say that furnace operators generally will heartily agree with Mr. Sweetser that the improvement in the quality of the coke and blast-furnace operation, generally, has far more than compensated for the increased amount of silica which has occurred in the ores in recent years. Mr. Sweetser did not bring out all the arguments in favor of this, but a careful reading of his paper will show that of the two furnaces compared, the actual yield of the Columbus furnace was much better than that of the Dover furnace, which was quoted as typical of operation, when the coke was not of such good quality. One important reason for that better furnace practice lies in the better quality of the coke. The difference in value between low-ash coke and high-silica ore cannot be measured merely by the amount of slag they produce. Better quality of coke and better furnace practice have resulted generally in much smoother furnace operation and much more complete recovery of the iron from the ore.

I was also much interested in Mr. Joseph's paper.[3] I happen to have had long association with Mr. Joseph on the subject of coke quality. He, in a more or less experimental way, and I, in a practical way, have been testing coke for a good many years. Although we had a few disagreements at first, I think we have about decided to agree that the coke-testing problem is fairly well settled. However, in applying a test for ore on the basis of the tumbling test for coke, not having read his paper, I was rather put out to know what he was trying to deduct from the results of his experiments. It might be too much to say that it sounded as though he were trying to get us some ore which would go clear through the furnace without being decrepitated or disintegrated. But certainly the results desired from ore and from coke are different. Generally one wants the coke to go through the furnace and arrive at the tuyeres with little diminution in the size of pieces, but it is necessary to reduce the ore almost completely before it arrives at the tuyeres. Mr. Joseph quoted and mentioned, particularly, the case of limonite. The figures he gave would tend to throw limonite

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[3] See page 365.

into rather a bad light. However, all furnace operators know (and I imagine it is information that most mining men have) that some of the limonite ores are in particular favor among the blast-furnace operators; partly, no doubt, because of their chemically combined moisture. He might give that fact consideration in drawing conclusions from his experiments along the line of ore testing, which, let me add, are certainly very interesting and may prove of great value.

R. H. SWEETSER.—Mr. Haven brought out something that I think Mr. Joseph can help us on. Mr. Joseph, you had the three furnaces. The No. 4 furnace at Illinois did not have as much reduction of ore on the third plane as the other two. What were the relative heights of the three furnaces?

T. L. JOSEPH.—The South Chicago furnace was slightly the higher, but I cannot remember exactly the difference in height. The height from the stock line to the tuyeres is given for the three furnaces in Table 1.[4]

R. H. SWEETSER.—Are you ready to say that it is possible to have some of the furnaces too high?

T. L. JOSEPH.—I did not say anything about the height of the furnace in my paper. It is really not the main point I was trying to drive at. My point was that there are lake-ore furnaces operating on excessive amounts of fine ore. We have found that these furnaces have very irregular gas distribution, that the gas is going three or four times as fast in the center of the furnace as it is along the walls. The whole blast-furnace process depends upon a countercurrent movement of ore and coke and stone and gas, and although the fine ore presents an enormous surface to the gases to heat the ore and to reduce it, it is mechanically impossible to blow the gases up through the fine ore.

We introduce coke, as Mr. Haven points out, to open up the charge so that the gases can get through and still the stock will settle. We had found that furnaces on coarse ores, such as the Holt furnace at Alabama, had a gas distribution that was much better, and that a larger proportion of the carbon reached the tuyeres and was burned there for generation of heat. We assumed that if the South Chicago furnace were operated on an ore mixture so that there would be as good distribution as in a Provo furnace, the operation would be improved. So we suggested in the paper some combination of sizing and sintering. At Provo, at first the ores were coarse. They were crushed down to past 2 in. and sized, and practice improved.

Mesabi ores are much too fine to start in sizing without sintering. It is useless to talk about it, because unless about one-half of the ore mixture is coarser than $\frac{1}{2}$ in., the sizing operation does not seem to be feasible. So our thought in this paper was that there are certain iron ores which, because they are fine already, or because they break down in the furnace, should be sintered. Very fine ores offer one case where sintering should be done; another is of ores that break down after they are charged in the furnace.

One ore that was on the slide this morning broke down on heating as well as on cold work. That ore is being sintered now. I understand that the furnace has shown a great improvement.

CRUSHING OF ORE

The important thing we have in mind is that in the blast furnace we are trying to preheat a large amount of iron ore, and trying to reduce it. The gas is generated at the bottom of the furnace. Obviously there must be contact between the gases and

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[4] See page 366.

the charge, to reduce it. If ores are too coarse it takes too long for the heat to penetrate into the ore, and reduction is slowed up. On the other hand, if the ores are too fine, the gas cannot be blown through them. The gas channels up through some porous section of the furnace. It seems to me that the gas distribution we have found in six or seven furnaces is so far from ideal that if we can work out some preliminary preparation of the charge that will produce a more uniform distribution of the gas, the furnace operation certainly ought to improve.

The tests that we made were devised simply to show which ores would break down more than others, and that the screen analysis of the ore as is does not indicate its behavior from the standpoint of furnace operation. You might have an ore that looked good from the screen analysis, yet in the furnace that ore might break down a great deal and be objectionable. There is no reason why the iron-ore business and the blast-furnace business are not large enough so that these matters can be studied. With some experimental work, these different ores can be checked out in practice, and I think some testing methods can be worked out. This work is only a starter and is more or less to open up the problem.

Answering Mr. Haven's question, of course we do not want the ore to be so big that it will get down into the furnace unreduced. Coarse ore and the oversized pieces in lake ores should be crushed, and the fines, the potential flue dust, should be sintered to bring the ore more to sizes that offer a reasonable amount of surface, and yet do not offer so much resistance to gas flow that the gas cannot be blown through the ore, and have the stock settle. In the Provo furnace, for example, the stock does not settle as well as it did before the ores were crushed and sized. I doubt whether the furnaces on the Mesabi ores would settle at all if there were uniform radial distribution of the ore so that the gases were forced up evenly through the furnace. I think they would hang. In fact, the pressure figures out to be about 45 pounds.

The furnace operators have worked out a scheme that will allow the stock to settle and get the best possible contact between the gas and the ore. All we are trying to do is to get some possible leads as to how the ore structure can be improved in order to reduce the ore in the top of the furnace, where it should be reduced.

There are four southern ores in that group. About five or six years ago I was talking to the plant manager who used two of those ores. The furnace foreman showed me pieces of one of those ores at the tuyeres, or he said it was one of them, and I could see these black pieces. His claim was that the ore was getting down to the tuyeres unreduced, and the other ore was satisfactory. It actually showed in the tests that we made that one ore broke down to about 30 per cent. of its original size. That was the coarse southern ore that was satisfactory. The other ore that he said he saw at the tuyeres, of which I saw the black pieces but did not actually know whether they were ore or not, broke down practically not at all.

In determining the extent of crushing, we certainly want to know whether the ore is going to break down in the furnace, and we want to know how fast it reduces. We know none of that today. We have no data to show the relative rate of reduction of our ores. We do not know how much they break down in the furnace. Some of these simple things, I think, will go a long way to solve the problem of how to treat ore.

We have split these same 34 samples into 8 or 10 sizes, and we are going to study their reduction. It seems we must have this information in order to know how to treat a particular ore. We should have some definite concepts or some indexes of ore structure and ore size. This paper is merely a start, I believe, in that direction.

Our tentative plan for studying reduction is to make a gas corresponding to bosh gas in the blast furnace. It is about 34 per cent. CO, and the rest is largely nitrogen and hydrogen. We are going to pass that gas through a bed of the ore, heated electrically, probably, at some definite temperature, and by having, say, 8 or 10 sizes of

the same ore, by the time we get through with some 30 ores we will know something about the relative rates of reduction of various iron ores. The work described in this paper is just a start toward finding how much ores break down and how much the oversized should be crushed, and to what extent the fines should be sintered. But it has to work both ways. If the ore is too fine, it should be sintered; if it is too coarse, it must be crushed. The southern ores, in general, could be crushed to advantage, as they are doing at Provo, although some of the ores, like the ones we tested, seem to break down to about one-half of the original size just through heating and a small amount of mechanical work.

Efficiency of Furnace

G. E. Rose, Chicago, Ill.—What was the relative coke practice in the South Works No. 4 furnace as compared with the Provo furnace?

T. L. Joseph.—The South Chicago furnace rate was about 1900 lb. on basic iron and the Provo was about 2000 lb. of coke on the same kind of iron.

G. E. Rose.—It seems rather paradoxical or seemingly contradictory to contend that a good gas distribution (as you say you had in the Provo furnace) is essential to efficient blast-furnace operation when you also report that the South Works No. 4 furnace, with a poor gas distribution, made iron on 200 lb. less coke per ton of iron than the Provo furnace.

T. L. Joseph.—It is not possible to point to any particular thing as the one thing that controls the efficiency of the furnace. There are so many variables that they all have to be taken into consideration.

My point was that No. 4 at South Chicago was operating at a coke rate of about 1900 lb. in spite of, and not because of, poor gas distribution. For example, anyone who has seen the coke at Provo knows that it is poor coke. It is small and breaks up easily. It is fairly high in sulfur. The coke is much poorer than the South Chicago furnace. The ore is denser. It broke up very little in our decrepitation tests. So it seems that crushing and sizing was a step in the right direction. The thing, of course, that we like to do is to get back to fundamentals as closely as we can.

We believe, as I say, that the man who runs the blast furnace making pig iron of certain silicon specification regulates the amount of coke. He changes the amount of coke to meet silicon and sulfur specifications. The reactions that introduce silicon in the pig iron and take sulfur out, go on in the bottom of the furnace, in the hearth. In order to have a high temperature in the hearth, it is desirable that all the carbon, or as much as possible of the amount charged, shall reach the tuyeres and be burned there to generate heat, rather than come part way down the furnace and be consumed by reaction with carbon dioxide in the gas stream. That is what happens if ore gets low in the furnace without being properly reduced. CO_2 liberated in the lower part of the furnace reacts with carbon and forms CO, and the carbon goes out of the top of the furnace in the gas and never gets down to the tuyeres where you want to generate heat required in silicon control and sulfur control.

The furnace at South Chicago burned about 73 per cent. of the carbon at the tuyeres, and the one out at Provo burned something over 80 per cent., as I recall. There are certain fundamentals of that type that we think are sound enough to really rely on. If the No. 4 furnace at South Chicago had had the same ore chemically, and if the structure had been improved so that a more uniform gas distribution could be obtained, that operation would have been better.

G. E. Rose.—Possibly this South Works furnace is capable of generating sufficient heat in the hearth by reason of having an extraordinarily high temperature in the hot

blast. I do not know whether it has or not. If so, considerable reduction by direct carbon reduction could take place, and still maintain enough temperature in the hearth to make good iron. If the furnace were operating on this basis, less coke would be required than if all the reducing were done by CO. In other words, 1 lb. of carbon used in direct reduction would reduce more iron than 1 lb. of carbon converted into CO by oxygen from the air and the CO used as the reducing agent, but, of course, I understand that will give a cooling action in the hearth. On the other hand, if sufficient heat can be supplied, if your furnace and stoves are good enough otherwise and you can stand for that direct reduction, you will get a lower coke consumption than if you reduce the ore entirely by CO.

T. L. JOSEPH.—That is my point. The South Chicago furnace is operating fairly well in spite of and not because of the poor gas distribution.

G. E. ROSE.—Maybe that "in spite of" is the better operation. I am questioning the conclusions that are apparently being drawn from these data on gas distribution. The fact that the furnace that shows the poorer gas distribution shows the better coke consumption creates a question in my mind as to whether this gas-distribution test is a real criterion of good and bad blast-furnace operation.

T. L. JOSEPH.—If you are not sufficiently familiar with these three furnaces to know that the Provo furnace has an inferior coke, and that the Alabama furnace was operating on much leaner ores, I can easily see where the case is not very strong for the gas distribution. I think we are all agreed that hearth temperature is needed in a blast furnace. The hot blast proves that conclusively. You realize that temperature to a greater extent if you bring the carbon down to the tuyeres and burn it, rather than bringing only some fraction of it down. That is really the way this thing works out. If the ore is not reduced in the top of the furnace, it means that the carbon is not burned at the tuyeres; it is picked up by reaction with CO_2 at some higher elevation and goes out with the gases.

C. E. WILLIAMS.—I agree with Mr. Rose that it is difficult to arrive at a satisfactory conclusion by comparing one furnace, such as the South Works furnace, with the Utah furnace, and that Mr. Joseph, to make his point more definite, should compare the operation of one blast furnace when using sized and unsized ore. Such results are available for the Utah furnace and show the effect of sizing.

The coke used in the Utah furnace was small and friable, so that running on an unsized burden, the gas distribution was poor, resulting in a condition similar to that in the South Works furnace.

Changing the Utah furnace over to sized feed resulted in a decrease in coke consumption of several hundred pounds per ton. Originally, on unsized feed, the coke consumption was about 2400 lb. per ton of basic iron. After experience had been gained in the sizing, and I think, perhaps, some time after Mr. Joseph made these tests, the coke consumption was reduced to a little over 1800 lb. per ton, not on any one run but as an average. So I think the results of the operation of this furnace alone confirm Mr. Joseph's conclusion that better gas distribution improves the efficiency of the coke consumption.

R. W. H. ATCHERSON, Gary, Ind.—I think I can explain what Mr. Rose has in mind, a point that seems not to be thoroughly understood; that is, as a practical blast-furnace operator, he appreciates the importance of using the highest blast temperatures practical. In all our modern blast furnaces, one of our greatest problems is to be able to carry the high blast temperatures effectively. The point he brings out is that the conditions at the South Works may have permitted the use of higher blast temperatures than could otherwise have been carried.

PRACTICAL BENEFIT OF TESTS

G. E. ROSE.—The only question in my mind is in regard to the practical benefit of the test that Mr. Joseph has made. We all appreciate his having made the test, and his endeavor to be of service to the blast-furnace industry. I can see just how he looks at it; *viz.*, that a blast furnace is a piece of apparatus in which you have the ore, coke and limestone descending, and the gases ascending for the purpose of reducing this ore, and at the same time generating sufficient heat at the bottom of the furnace to maintain satisfactory grades of iron; yet the data from the test are rather hard to explain, in that the furnace with such a poor gas distribution, as shown by these tests, showed up as the more efficient furnace in regard to coke consumption. The question in my mind is whether his gas-distribution tests are real criteria of an efficient blast furnace. Perhaps the furnace works a little differently from the manner in which we think it does.

I should like to go a little further and say to this group that for a small steel company we have done considerable on beneficiation of our ore, in the first place in a washing plant and just recently in the sintering of a portion of the ore from another mine.

Our action has been taken on the basis of beneficiating the blast-furnace operation. You might say that that is the reason for the beneficiation of all ores. But I will point out this fact, that prior to our beneficiating certain ore by washing, we could hardly operate the blast furnace at all with a high percentage of this ore, on account of the free sand in it—the free silica. In fact, in order to use considerable of this ore prior to our putting in the washing plant (I happened to be blast-furnace superintendent at that time), the only thing I could do to ameliorate the conditions was to put on more siliceous ore, but with silica in the form of a silicate, so as to make a still greater slag volume and thereby render the free sand less disturbing. So that our action in the beneficiating of this ore was done to make it a workable ore in a blast furnace. It really was not a workable ore before. The blast furnace would break out in the bosh and give us all kinds of trouble. We were not trying to size the ore or make it better looking as an ore, but simply to beneficiate the blast-furnace operation, an operation that was not feasible prior to washing.

The same thing has moved us to beneficiate the ore from another mine, or a goodly portion of it, by sintering. The sinter has had a wonderfully good effect on the blast furnace in which we use it. Of course, this particular portion of the ore from that mine contains about 19 per cent. of free moisture and about 9 per cent. of combined water, and therefore in sintering that ore we drive off about 28 to 30 per cent. of water, on which we do not have to pay freight to South Chicago. About 18 to 20 per cent. of the burden of our basic furnace is made up of this sinter, and it has benefited the practice materially.   •

Our thought was that the ore in the raw condition, with the combined water in it, did decrepitate in the top of the furnace. At any rate, it gave us a very dusty furnace; a furnace that threw out a lot of flue dust. Now with the sinter, using about 18 to 20 per cent. of it, we have a reduction of the flue dust to about one-third of what we had formerly. It results in so much less ore used per ton of iron that it gives us a reduction in the cost of pig iron on that furnace after paying for the sintering of this 18 or 20 per cent. of the burden.

It seems to me, therefore, from our viewpoint, that it depends a great deal on just the character of the ore as to the benefits of beneficiating the ore. In other words, if an ore runs only 40 or 45 per cent. in iron, and the silica is in the form of silicate, and the ore is all right structurally and is not particularly high in moisture (although it would give better blast-furnace practice, no doubt, to enrich the ore by some process, if possible, so that the iron content would be higher), it is a question as to

how much you can stand in increased cost for beneficiation of the ore and yet come out even on the blast-furnace costs, if the ore works at all satisfactorily in its raw state.

T. L. JOSEPH.—Mr. Rose mentioned that this particular ore contributed a considerable amount of flue dust. We tested that ore and found that it did break down considerably in the hot working test. Our point in working up these tests is to get some simple test that can be applied to give some advanced information. It seems to be a rather expensive method of trying it out in a blast furnace, if you can get any possible lead by simple test methods to point out which is the bad actor and check that with the furnace practice. It seems to me that you might get an answer a little sooner and probably a little cheaper if you can find the right test method.

LOW-TEMPERATURE REDUCTION OF ORE

W. H. SMITH, Detroit, Mich.—This item of beneficiating iron ores suitable for blast-furnace use is an important subject to our blast-furnace men who are straining their endeavors to make the production of iron more efficient.

The General Reduction Corpn., which I represent, is concerned in what is known as low-temperature reduction of iron ore producing a product that is reduced iron from low-grade or high-grade ores economically suitable for blast-furnace uses.

Many ores when so reduced may be readily separated from the greater part of their gangue and then briquetted into sizes suitable for blast-furnace practice and subject to all economies in melting and slagging. We have reduced ores from many of the largest deposits in different parts of the world, and in the majority of cases marked beneficiation is obtained by removing of gangue after reduction. We have reduced some of the soft Mesabi ores known as wash ores, whose natural iron content averages 46 per cent. We have removed 70 per cent. of the gangue after reduction. Some of this iron is very soft and fine, the apparent gravity ranging from 3.0 to 0.2, and briquettes into desirable blast-furnace sizes.

It was my privilege to conduct an investigation on the recovery of iron from lean ores some years ago, for one of the largest industrial concerns in this country. The results and economical regaining of iron from ores carrying 36 per cent. iron and over warranted their future dependence on such reserves for their supply of iron.

We feel that the time is not far distant when the blast-furnace man will insist that not only his charge be prepared in proper sizes but that the iron content be high and slag volume low in ensuring economical production. This will be obtained by the reducing and preparing of the iron before charged. We feel that when the blast furnace has the assistance of the ore-reduction ovens, as used in our method of preparing iron, its burden will not suffer by an excess of fines or slag; also, that our ore resources will have expanded in their fields of economic usefulness.

R. H. SWEETSER.—We are glad to have this angle from direct reduction. Fifty-seven years ago, at a meeting of the American Institute of Mining Engineers, this same direct reduction was presented to a group of blast-furnace men and iron-ore men. Sir Lothian Bell said he thought it was really almost (I won't say "quite") an insult to the blast furnace to say there was any more direct method than putting the ore into the top of the furnace and taking iron out at the bottom.

We are glad to have this viewpoint from Mr. Smith, because these processes are going to progress until we get a better way of separating the metal. A unit of iron and a unit of heat form the basis of the iron and steel industry. We are after a unit of iron with the least expenditure of a unit of heat.

It is very likely that the process Mr. Smith is working on may lead us along so that we will be getting not only more iron and cheaper iron, but better iron.

W. H. COGHILL, Rolla, Mo.—How is the silica removed from the iron? If the gangue is to be removed, how is it done?

G. B. WATERHOUSE, Cambridge, Mass.—I do not know just what Mr. Coghill has in mind, but I think I have a pretty clear idea of what Mr. Smith had in mind. He rather feels that beneficiating may have to go the whole way, that it will be necessary to reduce the iron ore right down to metallic iron, and then by means of the usual and simple and well understood methods of magnetic concentration get perhaps different grades of product. As he said, he had one product with a lake ore that ran 97 per cent. by magnetic concentration of the crushed reduced ore, and he had another material that ran, I think he said, only 40 per cent. iron, or something of that kind. So to answer your question directly, he is relying on magnetic concentration of the ore, reduced to metallic iron, and crushed.

T. L. JOSEPH.—Dr. Waterhouse, with an ore whose structure makes it difficult to separate the silica and the metallic or mineral particles, would you not have the same difficulty after reducing as before, because it would be just as hard to break the silica away from the metallic iron as away from the oxides?

G. B. WATERHOUSE.—That is plain common sense. If you reduced an iron silicate to metallic iron, it would be extremely difficult to remove the silica. It may be foolish to even think of a step like that. Maybe you would just have to use it in the blast furnace as it is and not try to work out some method of this kind.

G. E. ROSE.—I wonder if Dr. Waterhouse could tell us how Mr. Smith proposes to carry on this reduction.

G. B. WATERHOUSE.—I think the best way to answer that is that Mr. Smith is doing this work at Detroit. He calls his company the General Reduction Corpn. He has not attracted any publicity or given much publicity to it, but he is very willing to show anybody in the world what he is doing, if they will go to Detroit. It is being done there, mostly at the University of Detroit, which is a convenient place in which to carry out the experiments.
The process is a method of direct reduction. Most of his work has been done by mixing charcoal with the ore and charging it into his particular design of oven, which looks for all the world like a battery of coke ovens. The iron ore and charcoal are charged at the top by suitable means. It descends very quietly, just as it does when the blast furnace works nicely, and just as it does in the shaft of the blast furnace; it goes in cold and is gradually heated as it descends. Then it is discharged cold to the hand, at the bottom. It is very much like the old style Semet-Solvay or the present style of Semet-Solvay coke ovens so far as the arrangement of flues for heating is concerned. That may give you a rough idea of it. It just descends by gravity. I suppose the oven that he has takes a little over 14 hr., maybe 15 hours.

E. P. BARRETT, Minneapolis, Minn.—What size ore?

G. B. WATERHOUSE.—He has found a very interesting thing—that as a rule it is better to leave the ore in fairly good sizes. I think his best results have been obtained with about one inch. He started out with the idea that all the ore should be crushed, but he has come to the decision there are many ores that it is best to leave in a fairly decent size.

G. E. ROSE.—It comes out in a chunk that size?

G. B. WATERHOUSE.—It comes out that same size. Some expand, and others keep exactly the same size.

E. P. BARRETT.—Mr. Joseph mentioned some of the preliminary tests we are starting—that the tests indicate that the reduction to metal on −0.525 + 0.371-in. material in an atmosphere of practically pure CO at 975° C. for 1 hr. varies from 38 to 98 per cent. on this series of 34 ores.

Do not forget that all this reduced material absorbs sulfur, and the low-temperature process has no means of removal of sulfur from the material in the solid state.

G. B. WATERHOUSE.—I do not want to get into a discussion of sponge iron, but I have been associated with Mr. Smith almost since the beginning, and we have done many very interesting things. I think the best thing to do is to invite anyone who wishes to do so to go to see what he does. You should not make a positive statement about sulfur, because we have done much very interesting reduction work with high-sulfur reducing materials.

E. P. BARRETT.—To justify my position, I will say that I have been working on sponge iron for about five years myself, and my statement (I am like Mr. Sweetser) came as the result of my experiments, and I will stick to it.

G. B. WATERHOUSE.—My statement is from the same background.

W. H. COGHILL.—I asked my question about the removal of that gangue because it seemed to me that this magnetic separation would not be any simpler than other old, tried-and-true methods. Magnetic separation is old, to be sure, but we have other well established methods.

I have had a chance lately to study a few of the iron ores of the Mesabi district, and I think I can bring a word of cheer. The operators of the iron district are reputed for their ability to handle ore in large tonnage. They are famous the world over for their efficiency in that work. If they had studied the ore beneficiation that is applied to other districts and were as thorough in that as they are in their present work, I believe they would have much less trouble today in getting the material that they desire for the blast furnace.

The washing plants of that district are wonderful. Their methods of washing out the finest sands are marvelous. The bit of jigging that is done is very good. If the jigging were perfect, there would still be material that would require further treatment to remove this gangue, which I say can be removed at the plant just as easily as it can be removed from sponge iron.

In other districts where they are practicing concentration, the coarsest material is handled on jigs. The jigging in the Mesabi district is very good. I do not believe it would pay to spend much research to make it better. After that there is a jig tailing with too much iron in it. Also there are the natural fines that come from crushing, to make a jig feed.

In ore-dressing methods the country over, tables follow the jigs. I am well aware that the tables have been tried in the Mesabi district. I think it is a most unfortunate thing that the operators of those tables got the impression that they were not suitable. The tables have been removed. I am aware that some people talk about the small tonnage of the tables and the broad expanse of a table plant. What if the tables do cover a broad area? The ground you put them on is cheap. They are not built on city blocks where a big price must be paid for the ground. It seems to me that a table plant is not necessarily expensive. The jig tailings running more than 40 per cent. iron can be crushed to table size, and the fines can be tabled. The few products we have worked on cleaned beautifully. If the coarse part of the table tailings is given a gentle regrinding in something like a pebble mill, very clean products can be made. Possibly there are ores that cannot be cleaned so well, but if there are, the same difficulty would be faced in this matter of sponge iron;

if the gangue is so finely disseminated that it cannot be liberated in one way, it certainly cannot be liberated in the other.

Classification of the table feed has been sorely neglected. It was neglected in the early work of the Mesabi district. It has been neglected the country over. In our work at the Bureau of Mines we have given more time to the matter of classification of table feeds than any one thing. We have had a hand in remodeling a great many mills where classification was put in, and in every case it has made good.

As for the fineness of the material, that has to be considered. Of course, the blast-furnace man says, "What is to be done with the fine material?" I am not answering that except to say that sintering is coming in. We have worked on table concentration of those ores on tables of commercial size, on what we call quarter-size tables, and on the miniature table, a table only 15 in. broad and 30 in. long. In one of our recent tests, we took a Mesabi product running 41 per cent. iron and got 54 per cent. recovery of a grade of 62 per cent. iron and 7.5 per cent. silica. In the past we have worked back and forth between the laboratory and the mills. We do not hesitate to say that anything that can be done on the laboratory table can be done in a commercial plant.

We do not know yet the capacity of the tables. It is the heaviest material that I have worked on. The capacity will be relatively large.

We have accurate figures on the cost of running the tables. I was in a mill last Saturday morning where there are 114 tables running. It was a vast area, to be sure. I looked around for a man. Finally I saw one man bob up. I went over to him and said, "How many of you fellows are on this job?" The man replied: "I have a buddy." There were two men running 114 tables. I can tell you pretty closely what that work was costing. The ore was prepared, ground and put into the table room, and 4 c. per ton running cost was covering the cost of that table operation.

The Mesabi district has gone ahead with beneficiation. The work so far is splendid, but I think we need to take hold and copy from other districts. There are plenty of districts to copy from. The wonderful work that is done with tables was not developed in a day or in a year—it has taken years.

Benefit of Sintering Ores

F. A. JORDAN, Youngstown, Ohio.—I should like to introduce another phase in this discussion. There is a large tonnage of ores on the different ranges that contain from 20 to 30 per cent. moisture, and the question of sintering those ores has come up a number of times. It is argued by many that the only benefit that can come from sintering them is the saving in freight on the moisture, because of its reduction to nearly zero. From what Mr. Joseph is pointing out, maybe that is not the whole story. Perhaps the material used in the blast furnace without sintering would make so much fines that it would decrease the output of the furnace and at the same time very much increase the amount of flue dust. I take it that the question of whether an ore containing a large excess of water should be sintered might be centered on such experiments as Mr. Joseph is pioneering in.

MEMBER.—I was very much interested, Mr. Sweetser, in your comments on the splitting of the ores, separating the sizes. I do not believe you mentioned specifically at what point you thought it would be a good place to cut your ore. Could you elaborate on that a little?

R. H. SWEETSER.—I had no sizes in mind. Some one had mentioned the Hawkins ore, which is one of the "sweetest" ores to work in a blast furnace, I suppose, that a man ever used. We have been fortunate enough at our plant, The American Rolling Mill Co., to have that ore. Everything that comes out of the washer is

shipped. It occurred to me that somewhere there might be a division, I cannot say where. But I made that remark because the work being done by the U. S. Bureau of Mines in the filling of ores of different sizes separately has been a benefit to certain blast furnaces. We have had no practical experience along that line. But I do think, in view of what Mr. Coghill has just told us, that there ought to be a division somewhere in shipping the very fine stuff, instead of throwing it back into the regular run of shipment. There ought to be a practical line of demarcation somewhere. Does anyone here have anything to say on that subject?

Mr. Joseph spoke about sintering the finer sizes. I think they have decided in the Bureau of Mines that −14 mesh is the proper size to screen out and sinter. Am I right?

T. L. JOSEPH.—That is an indication of the amount of dust formed. The more of that material you get out by sintering, the less dust will be made in the furnace. In actual sintering operation it would probably work a little differently. If you were to sinter a really fine ore such as Mahoning, you would probably make a cut at 3/8 in. and sinter the material that was finer than 3/8, and charge the material coarser than 3/8 into the furnace. The amount of −14-mesh material is just an index of the amount of dust made. It is really not a general index of where to make the cut for sintering.

There are several ways that sintering and sizing can be carried out. For example, you might take the fines of several ores and sinter them, and charge them in with coarse fractions. But the cheapest way would probably be to pick some of the ores that we know dust excessively, sinter the finer sizes and mix the sinter and the coarser material. If there is any chance during the beneficiation of the iron ores to get a sized material, I think the iron-ore men and the blast-furnace men should get together and consider whether they should mix this nicely sized material back with some other ores to make a chemical grade, or whether they should actually ship that ore down to the furnace as sized material. In other words, I believe they might emphasize chemical grade a little too much. I think we talked about coke combustibility more than it deserved. It seems to me that ore structure should be considered. You want to get an ore with a good structure as well as a certain chemical analysis.

TREATING FINE ORE BY PROCESSES USED FOR FINE COAL

R. H. SWEETSER.—The question of taking care of very fine iron ore is just as important and very similar to taking care of the very fine coal dust. I know there are men here who have been working on that problem. We should like to hear from Mr. M. P. Walle of the Rheolaveur Company.

M. P. WALLE, Pittsburgh, Pa.—I am very new in the iron-ore fields and I cannot say much about the possibilities of using our process on the fine sizes because we are still in the experimental stage on very fine ores. The process has been used mostly on coal so far.

The difference between the work on Rheolaveur on the iron-ore field and Mr. Coghill's work in the field is that he had worked extensively on ores previously. We have not been able yet to produce with the process we are using the same results as on coal, because we have not yet all the necessary data to do so.

In my mind, the future units would embody a combination of high-capacity units of the Rheolaveur type (sealed discharge) with a roughing and a re-treating unit as may be seen in coal territory at the Pittsburgh Coal Co., with a gradual recrushing of the middlings and a re-treating of the fine tailings of this unit in free discharge units, to leave finally the very fine tailings to be re-treated either in a Rheo sludge unit or in another process like classifier and tables to get the last ore recoverable. (Since

the meeting, it has been found that the free discharge Rheo tailings contained rich ore under the 35-mesh size at the three commercial plants at Butler Brothers.)

But the results obtained up to now have not progressed as far as they should on the plants in use on the Mesabi Range; for this reason, I am reluctant to give figures, because they are not as good as they should be when all the data have been obtained. I maintain, however, that a combination of the Rheolaveur with high capacities down to a certain size material with an accurate method of recovering the very fine ore from the fine tailings will be the real thing. (When we secure the data on fine-mesh ores it will probably permit us to use at this point the sludge unit.)

The concentrating tables combined with preclassification require an immediate crushing to a very fine size, which we would not attempt for reason of cost.

I have been on the Range only one year and only on one property, but I have been assisted very much in my work by the company with which I am working. The problem is very different from the problem of coal, because one is just the reverse of the other, in that the spigot product in the ore fields is the merchantable product while in the coal fields the spigot product is the refuse or reject. It will be some time before we can publish operating data and operate the plants at full efficiency. I am convinced that the plants are not doing all they should now because of the lack of complete data; for instance, on gradual crushing instead of crushing all the material at once.

There is a limit in crushing, which theoretically would be very fine in size, but the practical solution would probably be to have first a roughing concentration of the crude with a separation and recrushing of the middling such as Mr. Hocking mentioned.[5]

We hope to be able to prove this next season on a sealed discharge plant. To date we have handled just one problem, the $-\frac{3}{8}$-in. ore in one unit; and the unit is not complete in itself. We tried to use this unit on a range of sizes for which it was not designed, for this unit should be followed by a second unit to work on the finest sizes of the tailings, then probably capacity and quality could be obtained both on tailings and concentrates. The unit was built to solve part of the problem and up to now we have not been able to connect to that unit the Rheo sludge unit which will be tried this winter.

The most interesting fact about Rheolaveur operation lies in the use of units of large capacities. Mr. Sweetser has seen our Pittsburgh coal plant and knows just what is meant. I see the future of the Rheolaveur plants in very large units working at high capacities, not trying to wash the tailings down to zero at once but progressively, down to a certain size determined by the range of washing permitted by the range of gravity of feed products as well as by the intermediate gravity of recirculating medium, returned to the apparatus, while a certain amount of middling would be separated and re-treated in a second unit of the same type. The tailings of this unit would be screened and the undersize re-treated in one or more free discharge units. The tailings of this unit would also be screened either on fixed screens or on vibrating screens, the undersize being re-treated in a sludge unit or in a combination of classifier and tables.

To do this, however, we must get the relation between cost and technical operation. Those are the figures we should have instead of straight technical data. Up to now all this has not been tied up together, although many of the men of the company with which I am working are studying that problem now.

We do not know whether the Rheolaveur will take care of the very fine ores as it does coal, but from technical data, we think it will. The question is, will it pay to do it? Cost data will solve that. A sludge unit on coal works down as far as

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[5] See page 364.

now required, about as well as the tables. The advantage of using the Rheolaveur on fine coal as against the tables is due to the capacity, which is much greater per unit. Mr. Bird made a comparison of tabling after classifying and Rheolaveur on the same coal and he found only a slight advantage in working with tables but commercially the Rheolaveur was doing as well because of its much higher capacity. The Rheo coal plants are washing down to 48 or 100 mesh, according to coal. Mr. Jordan, of Youngstown Sheet & Tube Co., can probably give you some information on the fine separation in coal by Rheolaveur.

F. A. JORDAN.—What I say, of course, will be rather offhand and from memory. The Buckeye Coal Co. has just completed and has had in operation for the past three months a plant that is washing coal under the Rheolaveur process and has been handling about 700 tons of −4-in. to 0 material per hour. The plant operates about 9 hr. a day.

Inquiry has been made about the fines. No washing or cleaning process washes very much of the inert material from the part of the coal, that is −48-mesh in size. In other words, 48 mesh is about the limit of washing with the prevailing processes.

Mr. Morrow, of the Pittsburgh Coal Co., is experimenting with froth flotation in the particular range of sizes below 48. The amount of 48-mesh material in the bituminous coal that comes from the Pittsburgh seam, of course, will vary with the character of the mine. If it is a captive mine that is producing coal entirely for by-product purposes, where the effort is not made to produce large coal, I think the system of mining is rather careless as to what the size shall be. I would say that about 8 per cent. is −48 mesh. Take a plant of 700 tons; 8 per cent. is 56 tons per hour, which is a considerable amount of that material to handle. It is one of the very serious problems of washing coal, what to do with the −48 mesh. It is very simple to put it into a Dorr thickener and thicken it down to about 45 per cent. solids, but after that, what? That is the serious part at the present time in the washing of coal, whether it is washed by jigs or tables, Rheolaveur or what not.

A number of schemes are being tried. One is to include that material with the larger material, say the −⅜ material and put it through the Carpenter centrifugal dryer. But what happens there is that some of the fines goes with the water and returns in the circuit; it just travels around.

Another scheme is to put this on top of the fine coal which is carried in a great big dewatering elevator, such as the plant of the Colorado Fuel & Iron Co. at Pueblo. That has for its merit the feature of simplicity and it works fairly well.

In the plants of the Pittsburgh Coal Co., they are actually using vacuum continuous filters, but the trouble there is that when it has been filtered, it still has 20 per cent. moisture, and then what can be done? The first and only thing one can think of is the heat dryer, but if such fine material is put into the heat dryer, it just gums up the dryer. The next thing is to put in coarse coal to make the fine coal travel. Then the capacity of the dryers must be increased, because there are not enough dryers, and the sludge is just going around in a circle, as I see it, in the present development of washing.

I rather think that the fines in the iron-ore washing are much the same thing. They can be separated. I am not entirely in agreement with Mr. Coghill about the table. I think perhaps if it is −200 mesh, a drag or bowl-type classifier will do almost as good a job more cheaply. But until somebody can tell us how much sinter in the blast furnace is worth to us, we are confronted by that problem more seriously than just simply to capture the fine iron ore. If it is put into the furnace, it blows out of the top, and if you keep putting it in, it will keep blowing out. You have to do something with it. It might be a matter of chasing a good dollar with a bad dollar. I should like to have someone tell us how much sinter is worth to the blast furnace,

then we can answer all of the questions that Mr. Coghill has brought up and that others have discussed.

DECREASE IN FLUE-DUST LOSS

W. A. HAVEN.—I have been waiting for someone else to do it, as I did not want to pass the bad news around, but it seems no one will. Somebody ought to issue a word of caution to those who have their hopes bound up in the sintering of fine ores.

I think the beneficiation men and mining men should know that, due to the very great improvement in the physical quality of the coke and the general betterment of blast-furnace practice, the losses in flue dust have been coming down so rapidly that they now play a much less important part in the determination of pig-iron costs.

Only a few years ago common practice in flue-dust production was about 450 lb. per ton of pig iron produced. Some steel-plant furnaces today profess to be producing less than 100 lb. per ton of pig iron produced, which is only about 2.5 per cent. of the ore charged in the furnace.

When it comes to sintering all the ores that pass through 14 mesh, you are going to have difficulty in catching up, on a commercial scale, to the efficiency which the blast-furnace men have attained in the treatment of fine ores. Personally, as a blast-furnace man, I think it is better to pay considerable heed to what Mr. Rose has said, that the application of sintering, and perhaps beneficiation in general, can very well, for the present time, be made largely to ores that obviously cannot be used in the blast furnace without serious difficulties, those very high in moisture or very high in loss on ignition, or low in iron and high in impurities; rather than to assume that you can sinter an ore which is objectionable only because it runs high in fines, say 10 to 15 per cent. through a 100-mesh sieve, and get by commercially. The cost of sintering such ores at the ore mines, we are led to believe, is around $1.25 per ton. Sintering blast-furnace flue dust has reached a point where it has been done for 70 c. per ton. Those figures must bear consideration.

F. A. JORDAN.—I should like to hear Mr. Haven speak about the Dovel furnace.

W. A. HAVEN.—I do not believe that needs any particular discussion. The results obtained on many furnaces generally operating on fine ores show that they have done very good work. The Dovel construction has been fine.

What we are chiefly interested in, I think, is that many furnaces in this district, on the general average, are working on 85 per cent. of Mesabi ores. The ones that I referred to I believe have an ore burden of about that nature. Those furnaces have reduced their flue-dust losses in general, I might say, to less than 250 lb. per ton of pig iron, and in exceptional cases, which point the way to future practice, to less than 100 lb. per ton.

T. L. JOSEPH.—Do they still keep up the rates of blowing?

W. A. HAVEN.—In general, the rates of blowing have been kept up to or in excess of previous practice. Rate of blowing is largely dependent on other commercial considerations, particularly the demand for tonnage.

TREATMENT OF FINE ORE AFTER WASHING

R. H. SWEETSER.—Mr. Swart, what are you going to do with the very fine iron ore that comes out from washing?

W. G. SWART.—I do not think there is any great necessity for screening that out, if you take it out of the washing plants at the bowl classifiers. If it is to be kept

separate, it should be done right there and shipped separately, but I do not see how you are going to ship the fine ore full of moisture. You cannot get it through the cars or through the docks. Therefore, if you are going to save the fine ore separately it has to be prepared at the mine in some way. It is nothing but a sludge, nothing but a mud. At one time they tried to ship fine magnetite concentrates from Norway and Sweden to England, and they lost two of the boats. When the boats would roll, the cargo of concentrates would shift, and finally the boats capsized. That was a good many years ago. We looked into the possibility at Babbitt of shipping the fine wet concentrates. We came across the old story and we decided it could not be done, that whatever was done in the way of fitting it for the furnace had to be done at the mine before shipping. Sintering can be done at the furnace where there is furnace gas, and flue dust carrying an excess of coke, to mix with the ore, for less money than it can possibly be done up on the range, where all the coal must be brought in, but I do not have any definite answer for this problem.

T. B. COUNSELMAN, Chicago, Ill.—With the improved blast-furnace practice, the fine iron ore can be absorbed, which was not possible before. If that is true, I wonder why the blast-furnace people keep on insisting on such a low percentage of −100-mesh material. That is a serious detriment to the iron-ore operators, because you can go to almost any washing plant on the Mesabi Range and recover a great deal of very fine, high-grade iron from the present tailing of those plants; as Mr. Coghill put it, by well-known and well-tried methods. Flotation also can be added, because much of this iron is −200. The problem has always been, what are you going to do with it after you get it? The blast-furnace people say they do not want it. The iron-ore operators are required to keep the 100-mesh material in their shipping products below a certain figure. Therefore they cannot absorb this −200-mesh or −100-mesh material in their shipping product, and apparently the only answer is to sinter it. That would not pay in any one individual mine or any one individual washing plant, because the quantity of the −100-mesh material that could be recovered would not be sufficient to warrant a sintering plant. If the blast-furnace practice is so far improved that it will take care of many more fines, why would it not be permissible to ship that right in with the present material and take care of it in the blast furnace? That would greatly improve the metallurgy in the washing plants, because, while they recover up to 90 per cent. of the iron units now, they could recover an additional 3 to 4 or 5 per cent. if permitted to recover the very fine particles of iron.

SINTER FOR BLAST-FURNACE USE

W. A. HAVEN.—I do not wish my remarks to be interpreted as implying that sinter is not a preferred blast-furnace material. Someone asked for an evaluation of sinter. I doubt if the blast-furnace men present would attempt to state the premium that should be paid for sinter, but I think they will agree that, as compared with fine ore, a certain percentage of good sinter, particularly sinter from ore, is much to be preferred.

As to how they shall handle this sludge from the wet washing of ores, I am not prepared to say what that will result in, although Mr. Counselman's suggestion may be one way out. Not knowing the amount of it, it might be hard to say, but sinter is well liked by blast-furnace men generally, up to a certain percentage.

I made my previous remarks chiefly as a word of caution to those who are going into any beneficiation processes that involve sintering, or those who propose to screen out the enormous amount of fines in the general run of good Mesabi ores. They will have a serious commercial handicap to overcome, due to the improvement, generally, in blast-furnace practice in the use of finer ores.

T. L. JOSEPH.—I do not know that this is such a serious handicap as it might be. It does not cost much to screen ores and size them. I believe that something like one-third of the ore required to make a ton of pig iron can be treated, and the fines sintered, for around $1. When you consider that there is a possibility of increased tonnages, decreased dust loss and better quality of iron, through improved working of the furnace, the necessary saving with sintering does not seem like an enormous thing. It is a thing that should be worked out gradually. People are starting to sinter iron ores. Nobody is going to spend much money on sintering until he feels his way along. People sintering iron ore are coming to know the value of sinter. I think the thing has a good chance to work out because of the fact that there is a chance to improve the tonnage of the furnace, and the quality of pig iron. After all, the blast furnace has done wonderful things in the way of increased tonnages. We have our large furnaces. I think that with an improved ore burden physically, we can go much farther in the way of tonnages and cutting down costs. I do not pretend to know blast-furnace costs, but I do not believe the sintering and sizing of lake ores is such an enormous thing as it might appear to be. When one-half of the material in the burden is coarser than ½ in., there is a good possibility of sizing and sintering. When you screen out the fines and add the sinter to the coarse material you change the structure of the ore quickly. It does not mean sintering all of the ore, but something like one-third of it.

F. A. JORDAN.—In relation to Mr. Haven's discussion about the furnaces making such a showing in reducing the amount of flue dust, I should like to suggest that maybe it can be accounted for partly in another direction. All of the beneficiated ore, or a very large portion of it, has been beneficiated in at least two ways. Beneficiation has reduced the amount of silicon and it has very much reduced the amount of fine material that is being shipped to the market. I submit that if that beneficiated ore is 30 per cent. of the total tonnage, should not the reduction of the amount of fines that are blown over by the furnace be reflected partly because of that, rather than take full credit because of some improvement in the blast furnace? On the other hand, the blast-furnace men have been increasing their pressures, I believe, in the same period of time during which the ore producers have been reducing the amount of fines that are actually shipped down the lake.

R. H. SWEETSER.—Is any blast-furnace man willing to admit that our blast-furnace pressures are higher than they were 15 years ago, or during the World War?

G. E. ROSE.—I do not think that the blast pressures are higher. I think Mr. Jordan means that the cubic feet of blast blown per minute is greater. I think, as Mr. Haven said, all blast-furnace men will agree that sinter is a preferred metallic material for a blast furnace. The only question is, how much is it going to cost to make this sinter? In our work, of course, as I stated before, we are sintering an ore that carries a great percentage of moisture, natural and combined. Therefore, the saving in freight, due to the sintering, is material, and goes a long way in counteracting the cost of sintering. Therefore, with the material going into the blast furnace in better shape, it works out as an economical process to sinter such ore.

When you come to an ore that works satisfactorily without being sintered (even though it is fine), except for the increased flue dust that is produced from such an ore, and if such an ore is fairly low in moisture, about 10 to 12 per cent., the economical and commercial operation of the blast furnace is a little different matter, because there is not nearly as large a saving in freight, and there is just as much cost for sintering. Therefore all of the sintering cost that is not taken up by less freight on lower moisture must be regained from better blast-furnace operation, in order to come out even. Of course, what Mr. Jordan has asked is just how much that better

blast-furnace operation amounts to. It is not within our experience really to state such a figure on ore that is simply fine and otherwise satisfactory to the blast furnace. I would say the margin of benefit to the blast furnace is considerably less in such a case than in our case, where the ore did not work satisfactorily in the blast furnace on account of the high natural moisture and high combined moisture, and, no doubt, due to the decrepitation mentioned by Mr. Joseph, making the ore in its raw state an unsatisfactory blast-furnace material; consequently, the benefits of sintering were on the right side of the ledger.

The point I would like to make is simply this: that the benefits to be derived from the beneficiation of iron ores for use in a blast furnace depend very largely upon how detrimentally the *raw ores* work in the blast furnace. In the beneficiation of one of our ores, the thing that moved us to action was not only the low iron content of the raw ore, but the fact that the raw ore would not work at all satisfactorily in the blast furnace on account of the free silica or sand content that it carried with it in the natural state. This, of course, was readily removed by the concentrating or washing process and at the same time made a very acceptable ore from the blast-furnace man's standpoint, both as to iron content and as to its freedom from fines, but if this raw ore had been a good working ore in the blast furnace without washing, even though the iron content was what it was in the raw state, I dare say that we might not have gone to the concentrating or washing process so quickly.

In other words, this was done to eliminate a very objectionable feature of the ore from the blast-furnace operator's standpoint and not simply to enrich the ore. Likewise, with another beneficiating process that we have adopted—that of sintering a certain grade of ore from one of our mines on account of its high moisture content and especially the high combined water content of approximately 10 per cent., making a total moisture content of approximately 30 per cent. This ore in its raw state worked unsatisfactorily in the blast furnace; hence we were moved to take action for its improvement, and naturally, on account of the possibility of eliminating the high moisture content and thereby not being obliged to pay freight on a large amount of water, we adopted the sintering process of beneficiation.

This elimination of the freight on the moisture goes a long way toward counteracting the cost of sintering and making the cost per unit of iron at our South Chicago dock *in the sinter* not very much in excess of the cost per unit of iron in the *raw ore*.

When we come to consider the beneficiation of an ore that works satisfactorily in the blast furnace, except for its fineness, and which carries only about 10 or 12 per cent. moisture, we have an entirely different proposition; or when we consider the beneficiation of an ore that is rather low in iron content, say, 46 to 48 per cent., but otherwise works satisfactorily in the blast furnace, we have quite a different proposition in the commercial advantage to be obtained by either concentrating or sintering such an ore. Hence, the problem of beneficiating low-grade ores of the Lake Superior district that have no real objectionable feature from the blast-furnace operator's point of view, except possibly their low iron content or the rather high percentage of fines, is a doubtful proposition from a commercial point of view with the present prices of ores. Of course, when iron-ore reserves become much more limited and the price for the iron-ore unit works higher, then the low-grade ores, no doubt, would stand the sintering expense and still work out favorably from a commercial point of view.

F. H. WILLCOX, Chicago, Ill.—I am going to try to give you an arbitrary figure. Take an operation making about 700 tons of pig iron per day. In the charging there will be about 20 to 25 per cent. of sintered ores or dust. That would be, out of 1400 tons of ore, 350 tons of metallic materials being sintered. On the average, they do not get any less coke per ton of pig iron. In all of the cases, it happens that there is

not very good heat equipment, and no more heat can be obtained. I cannot say whether more heat could be used, but I presume it could. With sinter, 35 tons more pig iron is produced than without sinter. If you say you can make $2 per ton on pig iron, that is, profit (which is a fair figure over a period of years), there is $70 a day extra profit. If you divide that by 350 tons of sinter, you save 20 c. per ton of sinter. It probably costs you 75 c. a ton to make the sinter.

In these cases, they happen to be sintering flue dust, with some scale, with perhaps some ore. It works out all right there because stock dust or fresh dust is charged to sintering plant at $0.00 to $1.00 a ton. If one ran a sintering plant in such cases on ore, it is plain that it would not pay to that extent, because, obviously, the savings result from substitution of $1.00 dust plus $0.75 sinter cost, or $1.75 ore, for $4.25 ore.

If you want to consider the average practice around a good plant today, you have to look at this: A good plant produces 800 tons. It has good dust-catching equipment and is bound to have good washing equipment. It is bound to have a sintering plant; if it does not now have, it is soon also going to have a Dorr thickener. It does not matter too much whether you make 150 or 400 lb. of dust per ton of pig iron, because you are going to get that back, and you are going to run it through the sintering plant. Once you have that equipment, it is not going to cost you any more to run 400 lb. of dust around that equipment than 150 lb. As a matter of fact, your net cost of sintering may be less on the basis of 400 lb. of flue dust than on 150 lb. Further, given this equipment, one can really blow the furnace and produce a good tonnage, without worrying too much about the dust.

So, as a general proposition, as long as our ores stay the way they are today, and our plants are built with the equipment I have outlined, and there is no material differential between the price of what we call physically good ore and an ore that is not, it does not pay to sinter ore.

Abroad you can buy a very nice ore, physically, for about $4.50, and you pay about $3.25 for the fine ores. The coarse ores come from Spain and the fine ores usually come from Africa or Sweden. You can buy them for from $1 to $1.25 less, sinter them, and have an ore comparable to or better than your physically good ore. Over there, when they use the fine ores they make a poor go of it. I think the question of furnace lines, construction and blowing equipment comes in. I think the situation has to be looked at from a rather narrow standpoint. Mr. Rose brought out that point. When you consider it from the standpoint of the present or future benefi- ciation of lake ores, sintering is decidedly correct. Looking at it from the standpoint of average run of commercial ores we have today, I do not think there is much to be found in further classification and sintering of these ores.

R. H. SWEETSER.—That is very interesting information, Mr. Willcox, but do you mean that if you put 400 lb. of flue dust per ton of pig iron around that circle, it will cost no more than if you put 200?

F. H. WILLCOX.—Probably it will cost less per ton of sinter, assuming you have the equipment anyhow and are going to sinter.

R. H. SWEETSER.—How about the cost per ton of pig iron?

F. H. WILLCOX.—The only thing I can say about the cost of pig iron, whether you are recovering 400 lb. or 100 lb. of dust, is this: If you are making 400 lb. of dust, your iron product, of course, is apt to be more irregular unless you watch the rate at which you are making flue dust. Some people try to gage the amount of dust they make. If they get one-eighth or one-half car at each cast, they charge a little extra ore or coke accordingly. The more flue dust you make, the more irregular your product will be. You do have a factor of saving or lower cost, perhaps, on the quality

of pig iron, but this is undoubtedly balanced by ability to blow the furnace strongly without excessive cost due to loss, as long as flue-dust production does not reach a point where it is a sign of overburdening.

T. L. JOSEPH.—If by sintering flue dust the amount of sinter is increased to, say, 15 or 25 per cent., is that comparable to taking the fines out of the ores and coarsening up the structure? It seems to me that if you sinter the flue dust and charge the sinter with fine ore, the situation would be different from that in which you take the fines out, sinter them, and put the sinter in with the coarse material in the ores. Nobody, as far as I know, has done that. It is vastly different from sintering the flue dust and putting it in with the fine ore.

F. H. WILLCOX.—I cannot answer that question with any positiveness at all, but just taking a typical modern furnace, with good coke, I would not expect to find a very marked difference, especially if the sinter were segregated in charging.

T. L. JOSEPH.—Do you think that if you sintered one-third of the material, you might increase your capacity, say, by 15 per cent.?

F. H. WILLCOX.—As a fair guess, 8 to 10 per cent.

T. L. JOSEPH.—That is one item. You doubt very much if there would be much saving of coke?

F. H. WILLCOX.—Taking blast-furnace design, ores and the plant as they are today, I do not think you can get very much. It is true that in the East on the furnaces that were charging fine magnetite concentrates 10 years ago, and then sintering them to the extent of 85 or 100 per cent. of the burden, the output came up nearly 50 per cent. I know one case where the coke came down from about 2600 lb. on magnetic concentrates to around 2100 lb. on sintered concentrates; another where sintering fine concentrates in conjunction with furnace and heat equipment redesign saved coke, producing a coke rate of 1600 lb. Of course, that is a very different case from the practice in 90 per cent. of the country on Lake hematite.

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